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# Syntheses of Organometallic Platinum(II), Platinum(IV), and Palladium(II) Complexes and Methyl Functionalization of 2-Methyl- And 2,7-Dimethyl-1,8-Naphthyridine.

Kevin J. Theriot

*Louisiana State University and Agricultural & Mechanical College*

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**Syntheses of organometallic platinum(II), platinum(IV), and  
palladium(II) complexes and methyl functionalization of  
2-methyl- and 2,7-dimethyl-1,8-naphthyridine**

**Theriot, Kevin J., Ph.D.**

**The Louisiana State University and Agricultural and Mechanical Col., 1989**

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300 N. Zeeb Rd.  
Ann Arbor, MI 48106

Syntheses of Organometallic Platinum(II), Platinum(IV),  
and Palladium(II) Complexes and  
Methyl Functionalization of 2-Methyl-  
and 2,7-Dimethyl-1,8-Naphthyridine

A Dissertation

Submitted to the Graduate Faculty of the  
Louisiana State University and  
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in partial fulfillment of the  
requirements for the degree of  
Doctor of Philosophy

in  
The Department of Chemistry

by  
Kevin J. Theriot  
B.S., Northeast Louisiana University, 1980  
August, 1989

For Jackie

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## Table of Contents

Acknowledgements . . . . .	iii
List of Tables . . . . .	xi
List of Figures . . . . .	xii
List of Schemes . . . . .	xiv
Abstract . . . . .	xv
Chapter 1. Syntheses and Characterization of Metalated and Cyclo- metalated Platinum(II) and Platinum(IV) C-Malonato Complexes . . . . .	1
Introduction . . . . .	1
History and Background . . . . .	2
Central C-Bonded $\beta$ -Diketones and $\beta$ -Ketoesters . . . . .	2
$\beta$ -Diesters as Ligands . . . . .	5
<i>O,O'</i> -Chelated $\beta$ -Diesters . . . . .	7
Central C-Bonded $\beta$ -Diesters . . . . .	12
C-Bonded Malonato Pt(II) Complexes . . . . .	20
Results . . . . .	21
Syntheses of C-Malonato Complexes . . . . .	21
Reactivity of Pt(II) C-Malonato Complexes . . . . .	24
Characterization of Platinum C-Malonato Complexes . . . . .	27
Proton NMR Spectroscopy of the Pt(II) Complexes . . . . .	34
Proton NMR Spectroscopy of the Pt(IV) Complexes . . . . .	40
Carbon-13 NMR Spectroscopy of the Pt(II) Complexes . . . . .	43
Carbon-13 of the Pt(IV) Complexes . . . . .	49

Infrared Spectra of the Platinum Complexes . . . . .	52
Structural Characterization of the Cyclometalated Pt(II) Complexes . . . . .	53
Conclusions . . . . .	65
Experimental . . . . .	65
General Comments . . . . .	65
Reagents . . . . .	66
X-ray . . . . .	66
<i>trans</i> -Dichloro-bis{methyl $\alpha$ -(methoxycarbonyl)[pyridine]-2- propanoate- <i>N</i> }platinum(II) . . . . .	67
<i>trans</i> -Dichloro-bis{methyl $\alpha$ -(methoxycarbonyl)[pyridine]-2- butanoate- <i>N</i> }platinum(II) . . . . .	67
Preparation of the <i>C,N</i> -chelates . . . . .	68
<i>trans</i> -Bis{methyl $\alpha$ -(methoxycarbonyl)[pyridine]-2- propanoate- <i>C,N</i> }platinum(II) . . . . .	68
<i>trans</i> -Bis{methyl $\alpha$ -(methoxycarbonyl)[pyridine]-2- butanoate- <i>C,N</i> }platinum(II) . . . . .	69
Preparation of Pt(dipy)Cl <sub>2</sub> , Pt(phen)Cl <sub>2</sub> , and Pt(diox)Cl <sub>2</sub> . . . . .	69
Dichloro-2,2'-dipyridineplatinum(II) . . . . .	69
Dichloro-1,10-phenanthrolineplatinum(II) . . . . .	70
Dichloro[1,1-bis(2-pyridyl)-1,3-dioxolane]platinum(II) . . . . .	70
Preparation of the <i>N,N'</i> -chelated <i>C</i> -malonato complexes . . . . .	71
bis(Dimethyl malonato- <i>C</i> )-2,2'-dipyridineplatinum(II) . . . . .	71
bis(Dimethyl malonato- <i>C</i> )-1,10-phenanthroline-	



platinum(II) . . . . .	72
Attempt to synthesize bis(dimethyl malonato-C)-[1,1-bis(2-pyridyl)-1,3-dioxolane]platinum(II) . . . . .	72
Reaction of Pt(phen)(dmm) <sub>2</sub> with Pt(phen)Cl <sub>2</sub> . . . . .	73
Reaction of Pt(phen)(dmm) <sub>2</sub> with acetyl or benzoyl chloride . . . . .	73
Reaction of Pt(phen)(dmm) <sub>2</sub> with methyl vinyl ketone . . . . .	74
Preparation of the dibromo Pt(IV) complexes . . . . .	74
<i>af</i> -Dibromo- <i>de</i> -bis(dimethyl malonato-C)- <i>bc</i> -2,2'-dipyridineplatinum(IV) . . . . .	74
<i>af</i> -Dibromo- <i>de</i> -bis(dimethyl malonato-C)- <i>bc</i> -1,10-phenanthrolineplatinum(IV) . . . . .	75
Preparation of the dichloro Pt(IV) complexes . . . . .	75
<i>af</i> -Dichloro- <i>de</i> -bis(dimethyl malonato-C)- <i>bc</i> -2,2'-dipyridineplatinum(IV) . . . . .	75
<i>af</i> -Dichloro- <i>de</i> -bis(dimethyl malonato-C)- <i>bc</i> -1,10-phenanthroline(IV) . . . . .	76
<i>cis</i> (Dichloro)- <i>bis</i> (dimethyl malonato-C)-1,10-phenanthrolineplatinum(IV) . . . . .	77
Attempt to synthesize Pt(phen)(dmm) <sub>4</sub> . . . . .	77
Reaction of Pt(phen)(dmm) <sub>2</sub> Br <sub>2</sub> with NaOH . . . . .	78
Chapter 2. Cyclopalladated Complexes of 2-Vinylpyridine	
Derivatives Possessing Pd-C <sub>sp<sup>2</sup></sub> Bonds . . . . .	79
Introduction . . . . .	79
History and Background . . . . .	79

Palladium and Platinum Complexes . . . . .	79
Ruthenium, Rhodium and Iridium Complexes . . . . .	88
2,2'-Dipyridine as a <i>N,C</i> -Chelate . . . . .	94
2-Vinylpyridine as a <i>N,C</i> -Chelate . . . . .	96
Results . . . . .	100
Syntheses . . . . .	100
Proton NMR Spectroscopy . . . . .	102
Carbon-13 NMR Spectroscopy . . . . .	102
Structure Determination . . . . .	104
Conclusion . . . . .	104
Experimental . . . . .	104
General Comments . . . . .	104
Reagents . . . . .	104
2-(2-Pyridinyl)-3-acetoxypromene . . . . .	104
2-(2-Pyridinyl)-3-hydroxypromene . . . . .	105
$\mu$ -Dichloro-bis[2-(2-pyridinyl)-3-acetoxypromenyl- <i>C,N</i> ]- dipalladium(II) . . . . .	106
Chloro[2-(2-pyridinyl)-3-acetoxypromenyl- <i>C,N</i> ]pyridine- palladium(II) . . . . .	107
Chloro[2-(2-pyridinyl)-3-acetoxypromenyl- <i>C,N</i> ]triphenyl- phosphinepalladium(II) . . . . .	108
$\mu$ -Dichloro-bis[2-(2-pyridinyl)-3-hydroxypromenyl- <i>C,N</i> ]- dipalladium(II) . . . . .	108
Chloro[2-(2-pyridinyl)-3-hydroxypromenyl- <i>C,N</i> ]pyridine-	

palladium(II) . . . . .	109
Chloro[2-(2-pyridinyl)-3-hydroxypropenyl- <i>C,N</i> ]triphenyl-	
phosphinepalladium(II) . . . . .	110
Chapter 3. Methyl Functionalization of 2-Methyl- and 2,7-	
Dimethyl-1,8-Naphthyridine . . . . .	111
Introduction . . . . .	111
Results . . . . .	114
Functionalization of 2,7-dimethyl-1,8-naphthyridine . . . . .	114
Functionalization of 2-methyl-1,8-naphthyridine . . . . .	116
NMR Spectroscopy . . . . .	119
IR Spectroscopy . . . . .	120
Experimental . . . . .	120
General Comments . . . . .	120
Reagents . . . . .	120
2,7-Bis(trichloromethyl)-1,8-naphthyridine . . . . .	120
2,7-Bis(methoxycarbonyl)-1,8-naphthyridine . . . . .	121
Attempted Reduction of 2,7-Bis(methoxycarbonyl)-1,8-	
naphthyridine with NaBH <sub>4</sub> . . . . .	122
2,7-Bis(hydroxymethyl)-1,8-naphthyridine . . . . .	122
Chlorination of 2,7-Bis(hydroxymethyl)-1,8-naphthyridine	
with PCl <sub>3</sub> . . . . .	123
2-Trichloromethyl-1,8-naphthyridine . . . . .	123
2-Methoxycarbonyl-1,8-naphthyridine . . . . .	125
2-Hydroxymethyl-1,8-naphthyridine . . . . .	126

Reaction of 2,7-Bis(trichloromethyl)-1,8-naphthyridine with KOH in EtOH . . . . .	127
Reaction of 2-Trichloromethyl-1,8-naphthyridine with KOH in EtOH . . . . .	128
Chapter 4. Synthesis of Metal Paddlanes. . . . .	129
Introduction . . . . .	129
Results . . . . .	129
Crystal Data . . . . .	131
Discussion . . . . .	131
Chapter 5. Hydrogen-Bonding in the Pyridine-Oxalic Acid System .	135
Introduction . . . . .	135
Experimental . . . . .	136
Dipyridinium oxalate-oxalic acid . . . . .	136
Dipyridinium bis(hydrogen oxalate)-oxalic acid . . . . .	137
Discussion . . . . .	138
Dipyridinium oxalate-oxalic acid . . . . .	138
Dipyridinium bis(hydrogen oxalate)-oxalic acid . . . . .	138
Chapter 6. An Improved Synthesis of 3-Methoxycarbonyl-4 <i>H</i> - quinolizone via Palladium(II) Assistance. . . . .	142
Introduction . . . . .	142
Experimental . . . . .	149
Dichlorobis(2-vinylpyridine)palladium(II) . . . . .	150
3-Methoxycarbonyl-4 <i>H</i> -quinolizone . . . . .	150
Summary and Conclusions . . . . .	152

Organoplatinum Complexes . . . . .	152
Cyclometalated Palladium Complexes . . . . .	153
Functionalization of Methyl Naphthyridines . . . . .	153
References . . . . .	154
VITA . . . . .	177
List of Publications . . . . .	178

## List of Tables

I. Selected analytical data for C-bonded $\beta$ -dicarbonyls . . . . .	29
II. Proton NMR spectral data for the Pt(II) complexes and comparison with the Pd(II) analogs . . . . .	37
III. Proton NMR spectral data for the Pt(IV) complexes . . . . .	41
IV. Carbon-13 NMR spectral data for the Pt(II) complexes and comparison with the Pd(II) analogs . . . . .	46
V. Carbon-13 NMR spectral data for the Pt(IV) complexes . . . . .	50
VI. Diagnostic Pt IR absorptions . . . . .	52
VII. Crystal data and data collection parameters for $C_{22}H_{24}N_2O_8Pt$ , $C_{24}H_{28}N_2O_8Pt$ and $C_{26}H_{30}N_2O_{12}Pt_2$ . . . . .	57
VIII. Important bond distances ( $\text{\AA}$ ) for $C_{22}H_{24}N_2O_8Pt$ and $C_{24}H_{28}N_2O_8Pt$ . .	59
IX. Important bond angles ( $^\circ$ ) for $C_{22}H_{24}N_2O_8Pt$ and $C_{24}H_{28}N_2O_8Pt$ . . . . .	59
X. Important bond distances ( $\text{\AA}$ ) for $C_{26}H_{30}N_2O_{12}Pt_2$ . . . . .	60
XI. Important bond angles ( $^\circ$ ) for $C_{26}H_{30}N_2O_{12}Pt_2$ . . . . .	60
XII. Coordinates for $Pt(C_{11}H_{12}NO_4)_2$ . . . . .	62
XIII. Coordinates for $Pt(C_{12}H_{14}NO_4)_2$ . . . . .	63
XIV. Coordinates for $Pt_2C_{26}H_{30}N_2O_{12}$ . . . . .	64
XV. Selected Bond Distances ( $\text{\AA}$ ) and Angles ( $^\circ$ ) for $[Cu(C_2H_3O_2)_2]_2 \cdot 2C_7H_7NO_2$ . . . . .	133

## List of Figures

1. Bonding Modes for $\beta$ -Diesters. . . . .	6
2. Effect of Stabilizing Ligands (L) on <i>O,O'</i> Chelates of $\beta$ -Dicarbonyl Complexes. . . . .	7
3. Use of $\beta$ -Diester Chelates in Synthetic Transformations. . . . .	11
4. Reactions of Organoplatinum Complexes. . . . .	24
5. Appearance of a Singlet, a Doublet, and a Triplet Coupled to Platinum. . . . .	28
6. Three and Four Bond Coupling Routes to C-3 for the <i>N,N'</i> -Chelates. . . . .	44
7. ORTEP Drawing of $C_{22}H_{24}N_2O_8Pt$ . . . . .	56
8. ORTEP Drawing of $C_{24}H_{28}N_2O_8Pt$ . . . . .	58
9. ORTEP Drawing of $C_{26}H_{30}N_2O_{12}Pt_2$ . . . . .	61
10. Cyclometalated Transition Metal Carbonyl Complexes of Pyridinyl Ligands. . . . .	94
11. Mechanism for Cyclometalation of 2-Vinylpyridine with $MX_2$ . . . . .	97
12. ORTEP drawing of $C_{28}H_{25}NClO_2PPd$ . . . . .	103
13. Interesting Examples of 1,8-Naphthyridine Complexes. . . . .	111
14. Syntheses of 2,7-Dimethyl-1,8-naphthyridine. . . . .	112
15. Proposed Mechanism for the Basic Hydrolysis of bis(2,7- Trichloromethyl)-1,8-naphthyridine. . . . .	118
16. Proposed Mechanism for the Reaction of 2-(Trichloromethyl)-1,8- naphthyridine with KOH and Comparison to the Haloform Reaction. . . . .	119

17. ORTEP Drawing of <b>185</b> . . . . .	134
18. Possible Bonding Modes in the 1:1 Pyridine/oxalic acid System. . . .	135
19. ORTEP Drawing of $2\text{C}_5\text{H}_6\text{N}^+\cdot\text{C}_2\text{H}_2\text{O}_4$ . . . . .	139
20. ORTEP Drawing of $2\text{C}_5\text{H}_6\text{N}^+\cdot 2\text{C}_2\text{HO}_4^-\cdot\text{C}_2\text{H}_2\text{O}_4$ . . . . .	141
21. ORTEP Drawing of $\text{PdCl}_2(\text{C}_7\text{H}_7\text{N})_2$ . . . . .	145
22. ORTEP Drawing of $\text{C}_7\text{H}_{11}\text{NO}_4$ . . . . .	147
23. ORTEP Drawing of $\text{C}_{11}\text{H}_9\text{NO}_3$ . . . . .	148



## List of Schemes

I. Functionalization of 2,9-Dimethyl-1,10-phenanthroline. . . . .	114
II. Synthesis of Metal Paddlanes. . . . .	129
III. Previous Syntheses of 3-Carboalkoxy-4 <i>H</i> -quinolizones. . . . .	142
IV. Proposed Mechanism for the Formation of 3-Methoxycarbonyl-4 <i>H</i> - quinolizone. . . . .	144

## Abstract

The syntheses of several new metalated and cyclometalated organoplatinum(II) complexes of *C*-malonato ligands have been accomplished. These complexes were characterized by  $^1\text{H}$  and  $^{13}\text{C}$  NMR and IR. The trans cyclometalated complexes utilized pyridinyl ligands possessing pendant groups at the 2-position with terminal malonate groups capable of forming either a five- or six-membered *C,N*-chelate. X-ray crystal structure determinations of these cyclometalated complexes were also done. The acyclic cis complexes are *N,N'*-chelates of dipyrindine or phenanthroline in which platinum is bonded to the central carbons of two different dimethyl malonate ligands. These *N,N'*-chelates were easily oxidized by either  $\text{Br}_2$  or  $\text{Cl}_2$  to give the corresponding Pt(IV) complexes; interestingly, this oxidation could also be accomplished by Cu(II) halides. The stability and reactivity of these complexes were also studied. A  $^{13}\text{C}$  NMR spectral analysis of the *N,N'*-chelates showed that when two paths for Pt-C coupling are available, the observed coupling constant is the sum of the two individual coupling constants.

Very few examples of cyclometalated 2-vinylpyridines have been reported, but, by the employment of  $\alpha$ -substituted 2-vinylpyridine derivatives, the synthesis of novel cyclometalated dimers was achieved. These dimers were readily cleaved by pyridine or triphenylphosphine and the structure of one of these monomers was proven by an X-ray crystal structure determination which showed the existence of the metal-alkenyl bond.

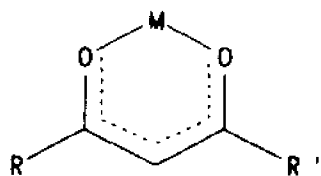
Methyl functionalization of 2-methyl- and 2,7-dimethyl-1,8-naphthyridine was accomplished by a three-step synthesis. The methyl group was first oxidized to the trichloromethyl group by *N*-chlorosuccinimide. Subsequent hydrolysis with

$\text{H}_3\text{PO}_4/\text{MeOH}$  gave the methyl ester which was reduced to an alcohol with  $\text{NaBH}(\text{OMe})_3$  which does not readily reduce less reactive esters. Because of the enhanced reactivity of the naphthyridine system, reagents [e.g.  $\text{H}_2\text{SO}_4$ , and  $\text{NaBH}_4$ , (and  $\text{NCS}/\text{CCl}_4$  for 2-methyl-1,8-naphthyridine)] that were used on other heterocycles could not be used on naphthyridine.

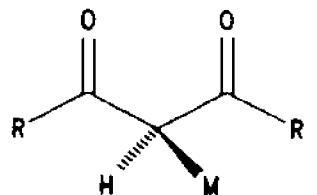
# Chapter 1.      Syntheses and Characterization of Metalated and Cyclometalated Platinum(II) and Platinum(IV) C-Malonato Complexes

## Introduction

Monoanions of  $\beta$ -diketones [ $\beta$ -dik(s)] [e.g. 2,4-pentanedione (acac), 1-phenyl-1,3-butanedione (bzac), and 4,6-nonanedione] and  $\beta$ -ketoesters ( $\beta$ -kes) [e.g. ethyl acetoacetate (etac)] are known to form complexes with diverse metals via a resonance stabilized six-membered  $O,O'$ -chelate **1**.<sup>1</sup> Although this is the most important mode of complexation, other types of complexation are known including  $O$ -unidentate,  $\eta$ -allylic, terminal- $C$ , and central- $C$  bonding.<sup>1c</sup> The last of these, central- $C$ -bonding **2**, is probably the second most prolific mode of complexation of  $\beta$ -dicarbonyls [ $\beta$ -dic(s)] outnumbered only by  $O,O'$ -chelates. Examples of central- $C$ -bonded  $\beta$ -dik or  $\beta$ -kes ligands are known for manganese(I),<sup>2</sup> rhodium(I),<sup>3</sup> rhodium(III),<sup>4</sup> iridium(III),<sup>1h,4a,5</sup> platinum(II),<sup>6 - 28</sup> platinum(IV),<sup>26,29 - 42</sup> silver(I),<sup>1d, 43-45</sup> gold(I),<sup>45,46</sup> mercury(II),<sup>1h,21,36,44,47- 57</sup> and palladium(II)<sup>14,16,18,58 - 72</sup> with most of the reports being done on Pd(II), Pt(II) and Pt(IV); thus, this discussion will focus on the Ni, Pd, Pt triad.



1

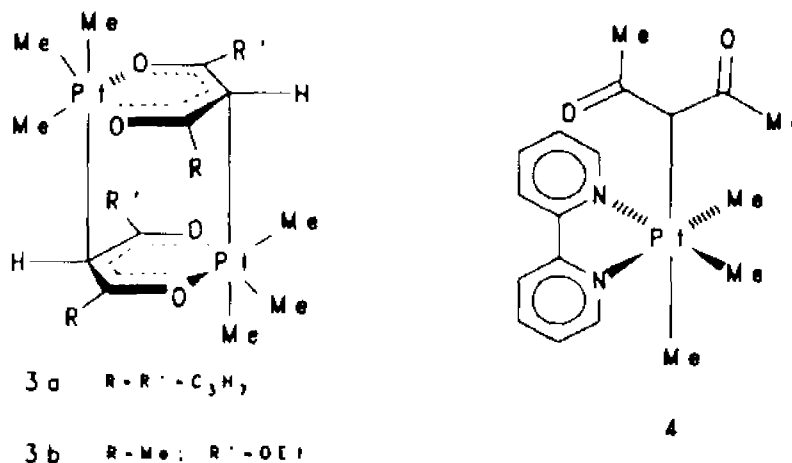


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## History and Background

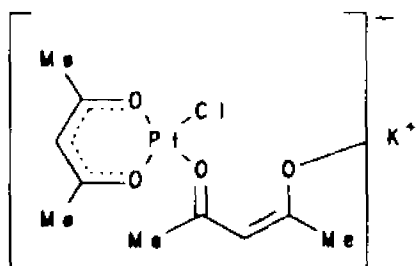
### Central C-Bonded $\beta$ -Diketones and $\beta$ -Ketoesters

The existence of central-C-bonded  $\beta$ -dicarbonyls was confirmed in 1960-1962 by Truter et al. through X-ray crystal structure determinations of  $[\text{Me}_3\text{Pt}(\text{C}_3\text{H}_7\text{COCHCOC}_3\text{H}_7)]_2$ <sup>31</sup> (**3a**),  $[\text{Me}_3\text{Pt}(\text{etac})]_2$ <sup>41</sup> (**3b**), and  $\text{Me}_3\text{Pt}(\text{acac}-\text{C}^3)(\text{dipy})$ <sup>32,35</sup> (**4**). In dimers **3**, the  $\beta$ -dics function as terdentate bridging ligands forming both a Pt-C bond and an  $O,O'$ -chelate; however, the  $\beta$ -dic in **4** is unidentate bonded solely through the central carbon.

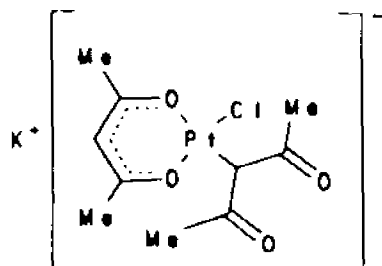


In 1901, Werner<sup>6</sup> reported the synthesis of the complex  $\text{K}[\text{Pt}(\text{acac})_2\text{Cl}]$  and over a half a century later Grinberg and Chapurskii<sup>73</sup> proposed **5** as the structure which involves one  $O,O'$ -chelating acac and one  $O$ -unidentate acac. Although one acac does form an  $O,O'$ -chelate as proposed, the fact that the other acac formed a Pt-C bond instead of a Pt-O bond remained unknown until the X-ray crystal structure determination was reported in 1962<sup>7</sup> proving **6** to be the correct structure.

The first example of a central-C bonded  $\beta$ -dic which did not have an oxygen ligand or a chelated ligand was the Pt(II) complex  $\text{Na}_2[\text{Pt}(\text{acac})_2\text{Cl}_2]$  (**7**).<sup>23,24</sup> This complex reacted with 2,4-dinitrophenylhydrazine adding further support to the proposed presence of the keto moiety.

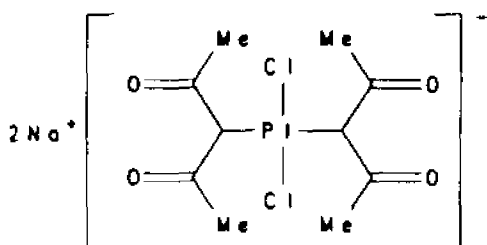


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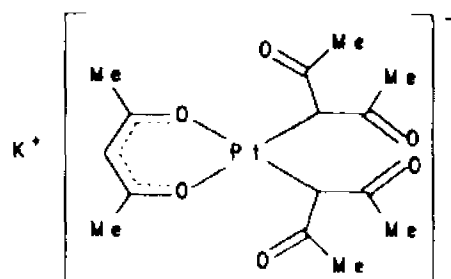


6

The interesting complex  $\text{K}[\text{Pt}(\text{acac})_3]$  (**8**)<sup>26,27</sup> is the only known complex of the Ni, Pd, Pt triad which contains only  $\beta$ -dic ligands with at least one central-C bonded  $\beta$ -dic. When **8** was treated with  $\text{HX}$  ( $\text{X} = \text{Cl}, \text{Br}$ ), greenish-yellow complexes resulted with compositions  $\text{C}_{10}\text{H}_{14}\text{O}_3\text{PtX}_2$  which were symmetric by  $^1\text{H}$  NMR spectroscopy possessing two different methyl groups, one aliphatic and one vinylic. In addition, the IR data indicated vinyl ether linkages as well as  $\text{Pt-X}$  bonds; there were no coordinated acacs. The complexes were monomeric in chloroform and non-electrolytes in nitromethane. In 1965, structure **9** ( $\text{X} = \text{Cl}$ ) was proven by Gibson et al.<sup>11</sup> who revealed that two acacs had condensed and eliminated one mole each of  $\text{H}_2\text{O}$  and  $\text{acacH}$  to give the dienyl complex **9**.



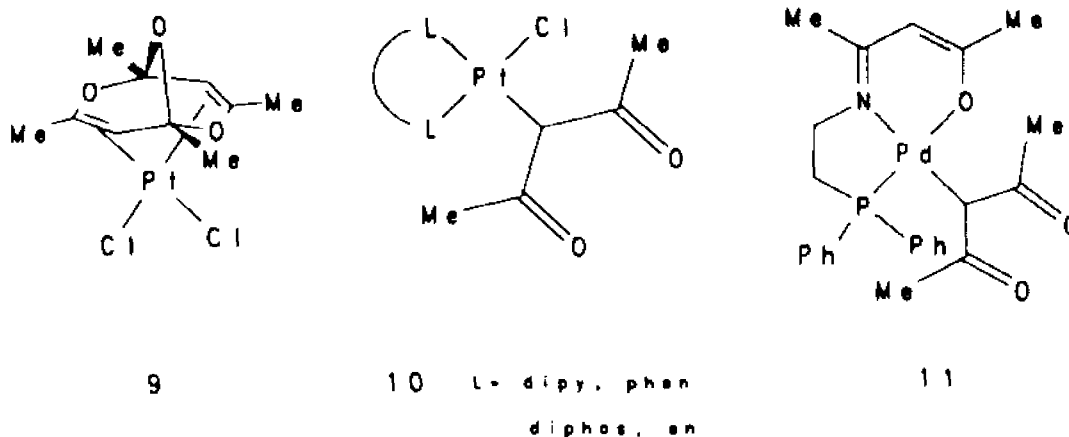
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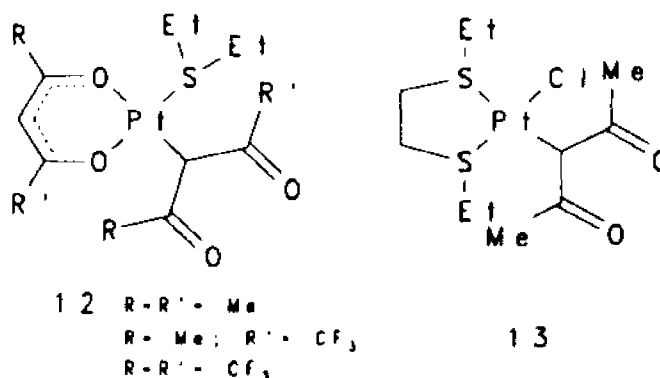
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The acid complex  $\text{HPt}(\text{acac})_2\text{Cl}$  was treated with bidentate ligands (dipy, phen, diphos, en) to give the neutral complexes  $\text{Pt}(\text{acac})(\text{L-L})\text{Cl}$  (**10**),<sup>22</sup> whose IR bands in the  $1600\text{--}1700\text{ cm}^{-1}$  region ( $\text{C=O}$ ) confirmed the presence of the C-bonded acac.

Hiraki et al. prepared unique tri-dentate *O,N,P* Schiff base ligands and formed the corresponding Pd(II) complexes which in turn reacted with acac to form the novel *O,N,P,C*-bonded complexes **11**.<sup>72</sup>

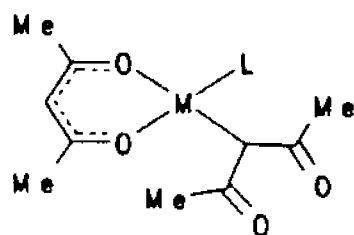


More recently *S*-ligands have been used to make  $\text{Pt}(\text{acac})_2\text{SEt}_2$  (**12**).<sup>21</sup> Thus by reacting *trans*- $\text{PtCl}_2(\text{SEt}_2)_2$  with  $\text{Ti}(\beta\text{-diks})$  in MeOH at 25 °C, the complexes  $\text{Pt}(\beta\text{-dik})_2\text{SEt}_2$  (**12**) were obtained. In the same manner, starting with a *S,S'*-chelated platinum complex  $\text{PtCl}_2(\text{S-S})$ ,  $\text{Pt}(\text{acac})\text{Cl}(\text{S-S})$  (**13**) was obtained.

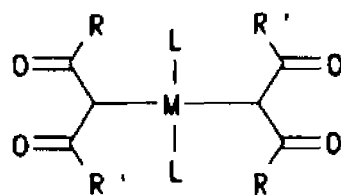


Reaction of the bis-chelate complexes  $M(acac)_2$  [ $M = Pd(II), Pt(II)$ ] with either *N*-monodentate ligands ( $L =$  alkylamines or pyridines) or tertiary phosphines gave *C*-bonded complexes  $M(acac)_2L$  (**14**) which had one *O,O'*-chelate and one *C*-bonded acac ligand.<sup>14,15,18,27,59,61,62,67</sup> It was also reported that reaction of  $M(\beta-dic)_2$  [ $M =$

Pd(II), Pt(II)] with an excess of L (py, 3-pic, 4-pic) gave  $M(\beta\text{-dic})_2L_2$  (15 and 16) which possessed two C-bonded acacs.<sup>15,27,70,71</sup>

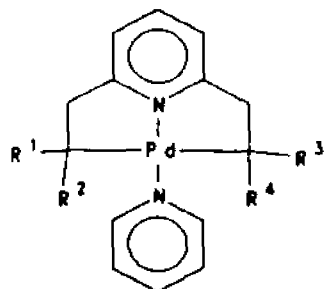


14 M- Pd, Pt  
 L- Me<sub>2</sub>NH, Et<sub>2</sub>NH,  
 2-, 3-, 4-picoline,  
 NH(CH<sub>3</sub>)CH<sub>2</sub>Ph, PEt<sub>3</sub>,  
 PMePh<sub>2</sub>, P(Cy)<sub>3</sub>, PPh<sub>3</sub>, py



15 M- Pt; R-R' = Me  
 16 M- Pd; R = Me; R' = OEt

Newkome et al. synthesized the novel complexes 17, which incorporated two  $\beta$ -dics and a pyridine ligand into unique terdentate ligand systems possessing two fused five-membered chelate rings.<sup>68,69</sup> The complexes were stable both in air and solution and none were found to interact with DNA. The external pyridine could readily be exchanged with 4-picoline.



17 R<sup>1</sup>-R<sup>2</sup>-R<sup>3</sup>-R<sup>4</sup>-COCH<sub>3</sub>  
 R<sup>1</sup>-R<sup>2</sup>-R<sup>3</sup>-R<sup>4</sup>-CN  
 R<sup>1</sup>-R<sup>3</sup>-COCH<sub>3</sub>; R<sup>2</sup>-R<sup>4</sup>-CO<sub>2</sub>Et  
 R<sup>1</sup>-R<sup>2</sup>-COCH<sub>3</sub>; R<sup>3</sup>-R<sup>4</sup>-CO<sub>2</sub>Et  
 R<sup>1</sup>-R<sup>2</sup>-COCH<sub>3</sub>; R<sup>3</sup>-CO<sub>2</sub>Et; R<sup>4</sup>-CO<sub>2</sub>H

### $\beta$ -Diesters as Ligands

Although there is a plethora of complexes of  $\beta$ -dik and  $\beta$ -kes ligands, there is one type of  $\beta$ -dic which has been virtually ignored in this area:  $\beta$ -diesters ( $\beta$ -des) [i.e. *dimethyl* (dmmH) and *diethyl* (demH) *malonate* esters 18 (R' = H)]. The two main types of bonding known for monoanions of  $\beta$ -des ligands are central C-bonded and O,O'-chelated; see Figure 1.



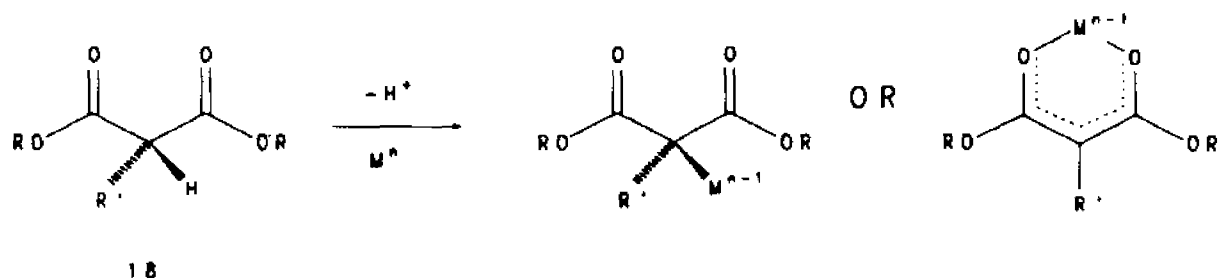


Figure 1. Bonding Modes for  $\beta$ -Diesters.

Kawaguchi<sup>1c</sup> has suggested that the formation of *C*-bonded versus *O,O'*-chelated complexes is directly related to the extent of keto-enol tautomerization of the free  $\beta$ -dik; thus low keto:enol ratios favor *O,O'*-chelation, whereas high ratios favor *C*-bonded complexes. Unsubstituted malonates have a relatively high "keto:enol" ratio and thus would be expected to form mainly *C*-bonded complexes. Despite this fact, there are as many literature reports of *O,O'*-chelated complexes of simple malonates as there are of *C*-bonded complexes; however, there are not many examples of either type.

The fact that malonates form both *O,O'*-chelates and central *C*-bonded complexes is probably due to a combination of two counter effects: 1) High "keto:enol" ratios disfavor *O,O'*-chelation, whereas 2) chelate stabilization favors *O,O'*-chelation. These two effects are apparently of approximately equal magnitude, and thus, when a system is sufficiently stable that chelation is not required, *C*-bonding takes place; however, where extra stabilization is needed, it is available through the *O,O'*-bonding mode.

The stability of the system is, of course, dependent on the other ligands. An interesting example of this can be seen in the  $\beta$ -dik systems  $M(\text{acac})_2L$ , which are prepared from the bis-chelates  $M(\text{acac})_2$ <sup>14,15,18,27,59,61,62,67</sup> (Figure 2). In the absence of stabilizing ligands, the needed stabilization of chelation in  $M(\text{acac})_2$  prohibits *C*-bonding; however when good donor ligands are added, *C*-bonding can occur.

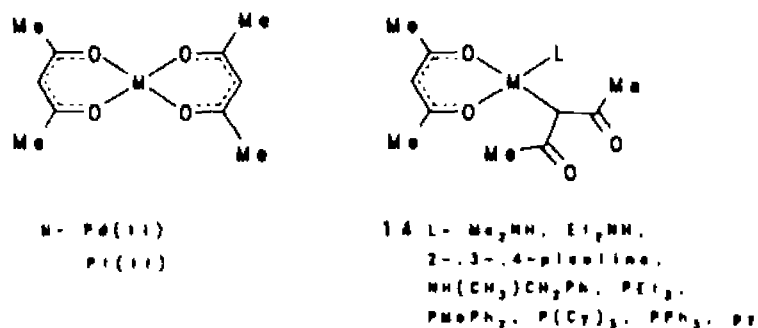
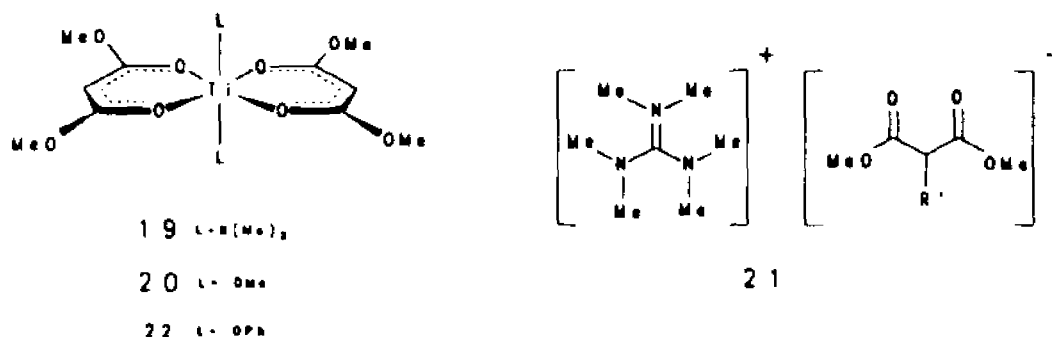


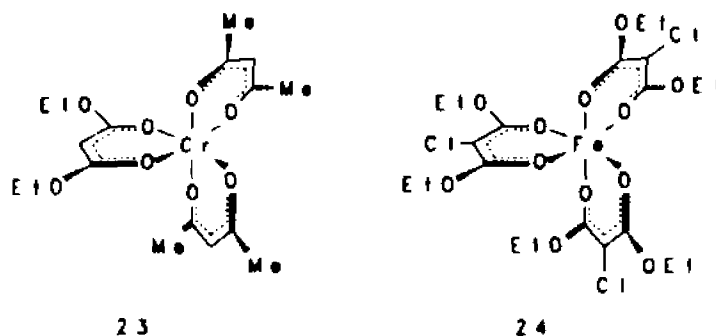
Figure 2. Effect of Stabilizing Ligands (L) on  $O,O'$ -Chelates of  $\beta$ -Dicarbonyl Complexes.

### $O,O'$ -Chelated $\beta$ -Diesters

Weingarten et al., in 1968, reported the syntheses of the first titanium malonato complexes  $Ti[N(Me)_2](dmm)_2$  (**19**)<sup>74</sup> and  $Ti(OMe)_2(dmm)_2$  (**20**).<sup>74</sup> The source of their malonate anion was the stable salt hexamethylguanidinium dimethyl malonate (**21**),<sup>75,76</sup> which would seem to be an excellent source of malonate anion for ligand exchange reactions but has not been exploited. The IR data for **19** and **20** were consistent with a  $O,O'$ -chelated structure (1643 and 1631  $cm^{-1}$ , respectively) although the  $^1H$  NMR spectra indicated the possibility of  $C$ -bonded malonates ( $\delta$  4.2-4.5). A similar complex,  $Ti(dem)_2(phenolate)_2$  (**22**), was reported in a Japanese patent.<sup>77</sup>



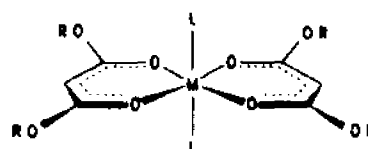
Synthesis of the mixed  $\beta$ -dic chromium complex  $[Cr(acac)_2(dem)]$  (**23**)<sup>78</sup> has recently been reported by the reaction of  $CrPh(acac)_2$  with Hdem in 50% yield. Benzene, the other product from the reaction, was obtained in quantitative yield but



no other chromium products were isolated. The  $O,O'$ -chelate of dem gave an absorption in the IR at  $1620\text{ cm}^{-1}$ .

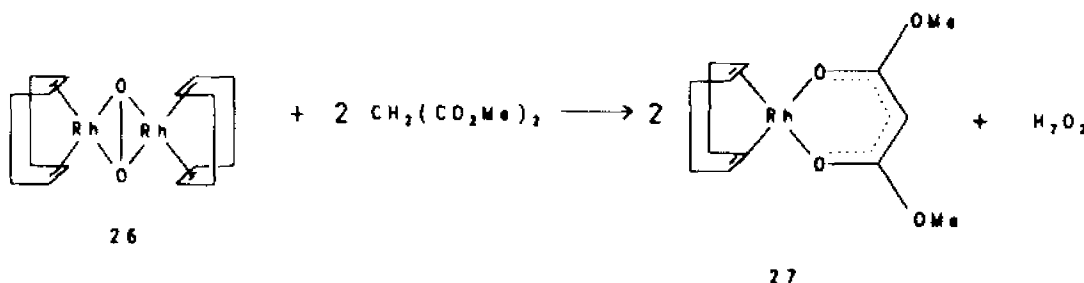
Diethyl dichloromalonate was found to undergo oxidative addition with  $\text{Fe}_2(\text{CO})_9$  to give  $\text{Fe}(\text{C}_7\text{H}_{10}\text{ClO}_4)_3$  (**24**).<sup>79</sup> The IR  $\text{C}=\text{O}$  stretch at  $1582\text{ cm}^{-1}$  in **24** is definitive for the  $O,O'$ -chelate, which is expected at longer wavelengths because the electron-withdrawing effect of the chlorine substituent decreases the keto:enol ratio<sup>1c</sup> and thus increases the propensity for  $O,O'$ -chelation.

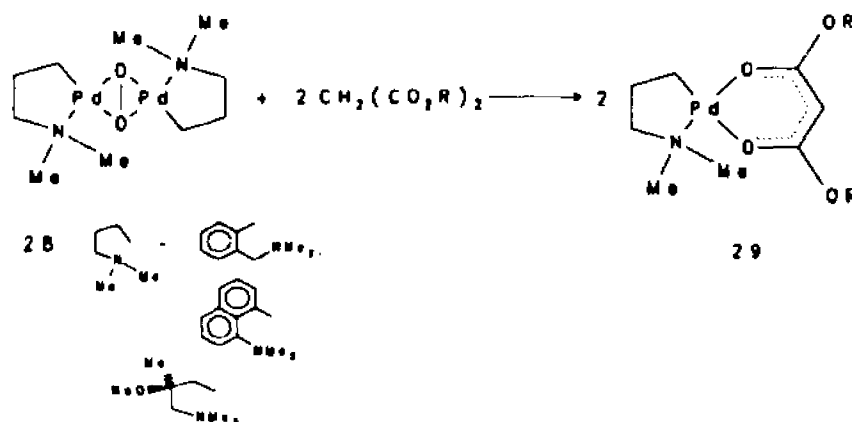
Both  $\text{Co}(\text{II})$  and  $\text{Cu}(\text{II})$ , with a variety of  $N$ -ligands ( $\alpha$ -pic,  $\gamma$ -pic, quin,  $\text{NHR}_2$ ), were found to form malonato chelate complexes **25**.<sup>80</sup> The IR  $\text{C}=\text{O}$  frequencies of **25** ranged from  $1610$ - $1625\text{ cm}^{-1}$ .



**25** L =  $\alpha$ -pic,  $\gamma$ -pic,  
quin,  $\text{NHR}_2$ ,  $\text{NHEt}_2$   
M = Co, Cu

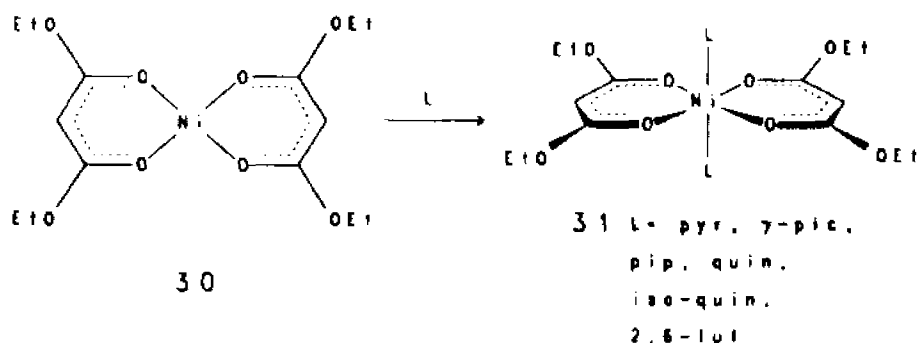
The interesting rhodium dioxygen dimer **26** was found to react with Hdmm to give  $\text{Rh}(\text{C}_8\text{H}_{12})(\text{dmm})$  (**27**) [IR  $1605\text{ cm}^{-1}$  ( $\text{C}=\text{O}$ )] and  $\text{H}_2\text{O}_2$ .<sup>81</sup> A similar reaction occurred





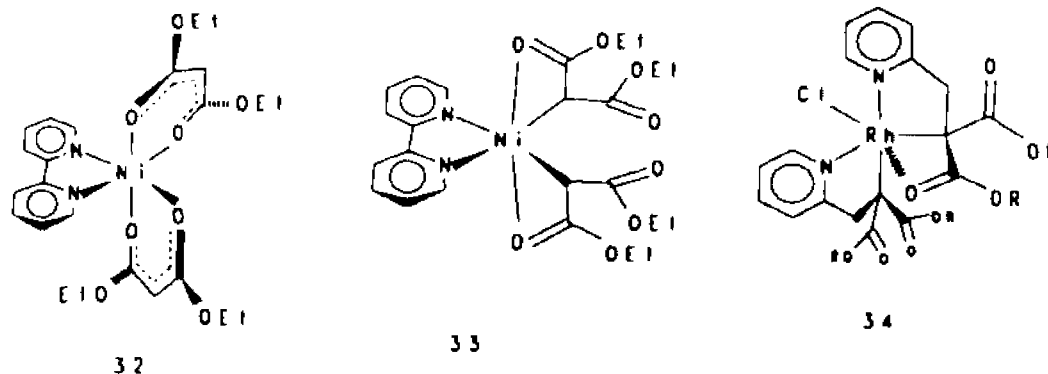
between the cyclometalated palladium complexes **28** and  $\beta$ -des ligands to give the cyclometalated complexes **29**.<sup>82</sup>

There are several literature reports on nickel malonato  $O,O'$ -chelates. Nickel chloride was found to react with diethyl malonate in the presence of aqueous  $\text{NH}_3$  to give the stable bis-chelate  $\text{Ni}(\text{dem})_2$  (**30**) which was then reacted with a series of bases to afford the mixed ligand complexes  $\text{NiL}_2(\text{dem})_2$  **31**.<sup>83</sup> The IR  $\text{C}=\text{O}$  absorption for **30** is at  $1600 \text{ cm}^{-1}$ ; whereas it ranges from  $1610\text{--}1630 \text{ cm}^{-1}$  for **31**.



The mixed ligand *tris*-chelated nickel complex  $\text{Ni}(\text{dipy})[\text{dem}]_2$  (**32**) was synthesized by two different routes starting with either  $\text{Ni}(\text{dipy})(\text{Et})_2$  or  $\text{Ni}(\text{dipy})(\text{COD})$ .<sup>84</sup> The mass spectrum of **32** showed a parent ion ( $m/e = 532$ ) and its octahedral geometry was implied by three bands in its UV spectrum ( $16350, 12930, 9630 \text{ cm}^{-1}$ ). However, the IR  $\text{C}=\text{O}$  frequencies ( $1660, 1675 \text{ cm}^{-1}$ ) appeared at slightly shorter wavelength

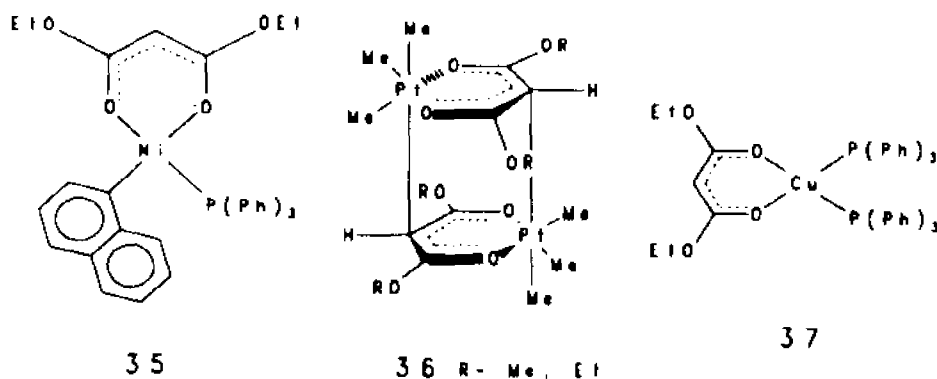
than for most malonato chelates which normally are in the  $1585\text{--}1640\text{ cm}^{-1}$  range. In view of this, another possible structure for **32** is the C-bonded **33** which incorporates C=O bonding similar to that observed by Newkome et al. for the Rh(III) complex **34**.<sup>4b</sup>



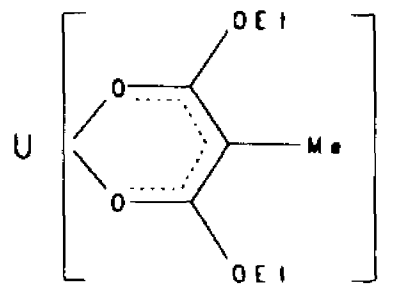
Agnes and Bart recently reported<sup>85</sup> the X-ray crystal structure determination of the chelated malonate Ni(II) complex  $\text{Ni}(\text{dem})(\text{naph})\text{P}(\text{Ph})_3$  (**35**), in which malonate was nearly planar (maximum out-of-plane distance  $0.067\text{ \AA}$ ) and  $O,O'$ -chelated.

In 1975 Kite and Psaila reported<sup>86</sup> the synthesis of the dimer  $[\text{Me}_3\text{Pt}(\beta\text{-des})]_2$  (**36**) in which the dialkyl malonate anion acted as a terdentate ligand as in  $[\text{Me}_3\text{Pt}(\text{etac})]_2$  (**3**); however, no conclusive data were reported.

Reaction of diethyl malonate with  $\text{MeCu}[\text{P}(\text{Ph})_3]_2$  gave the malonato chelate  $\text{Cu}(\text{dem})[\text{P}(\text{Ph})_3]_2$  (**37**).<sup>87</sup> The IR spectrum of **37** showed a C=O absorption at  $1643\text{ cm}^{-1}$  and the NMR had a singlet at  $\delta\ 5.12\text{ ppm}$ , both consistent with  $O,O'$ -chelation.



An interesting series of uranium(IV) complexes with the general formula  $UCp_n[\beta\text{-des}]_{4-n}$  ( $n = 0-2$ ) was reported<sup>88</sup> in which low temperature  $^1\text{H}$  NMR was used to study the fluxionality of the ligands. Included in the series was the dodecahedral tetra-chelated  $U(\beta\text{-des})_4$  (38).



38

Recently a copper(I) diethyl malonate chelate was used in the coupling reaction shown in Figure 3.<sup>89</sup> The copper malonate complex was not isolated and so it is not certain whether it is  $O,O'$ -chelated or  $C$ -bonded. The authors proposed initial nucleophilic aromatic substitution and cyclization to give 3-ethoxycarbonyl-2-oxo-2-indolizinyll Cu(I) which then dimerizes thermally to give the product.

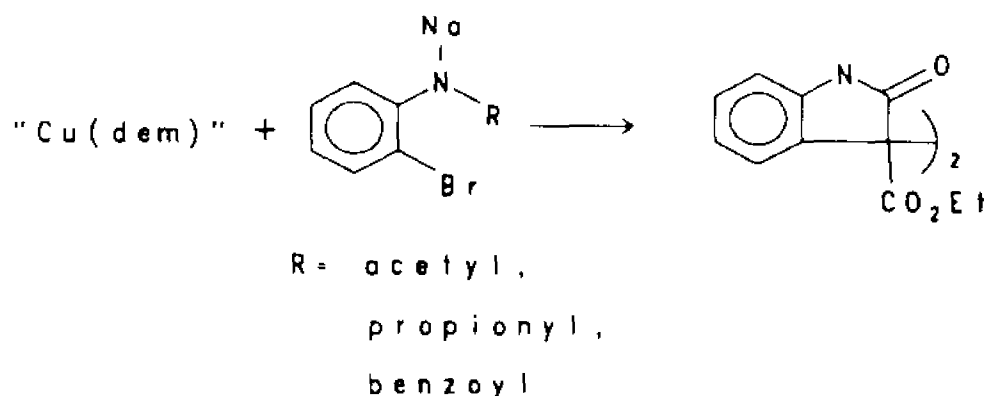


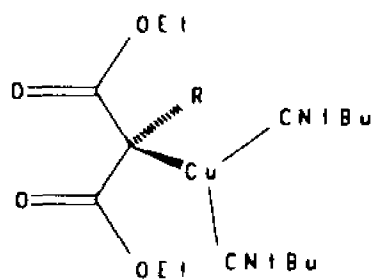
Figure 3. Use of  $\beta$ -Diester Chelates in Synthetic Transformations.

Zinc also forms complexes with malonates usually by oxidative addition into halo-malonates.<sup>80,90</sup> These complexes,  $XZn[CR(CO_2R')_2]$  ( $R = H, X, \text{alkyl}$ ), behave like Grignard reagents in terms of synthesis, stability, reactivity, et cetera.

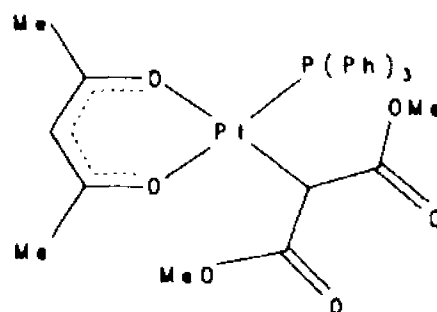
### Central C-Bonded $\beta$ -Diesters

The first examples of complexes which probably contained C-bonded  $\beta$ -des ligands were the copper(I) isonitrile complexes  $\text{Cu}(\beta\text{-des})(\text{CN}t\text{-Bu})_2$  (**39**).<sup>91</sup> Although the acac complexes were *O,O'*-chelated [IR (C=O) 1610  $\text{cm}^{-1}$ ], the malonato complexes appeared to be C-bonded [IR (C=O) 1690  $\text{cm}^{-1}$ ]. The  $^1\text{H}$  NMR for both types of complexes was reported;<sup>91</sup> however, the  $\text{CuCH}$  proton was not noted.

Ito and Yamamoto found that when  $\text{Pt}(\text{acac})(\gamma\text{-acac})\text{P}(\text{Ph})_3$  [**14**  $\text{M} = \text{Pt}$ ,  $\text{L} = \text{P}(\text{Ph})_3$ ] (which contains both a *O,O'*-chelated and a C-bonded acac) was reacted with dimethyl malonate, the C-bonded acac was displaced by C-bonded malonate to give  $\text{Pt}(\text{acac})(\text{dmm})\text{P}(\text{Ph})_3$  (**40**), as the sole product.<sup>20</sup> The product was characterized (IR) by its C=O absorptions (1740, 1715  $\text{cm}^{-1}$ ) and by  $^1\text{H}$  NMR. The chemical shift of the  $\text{PtCH}$  proton was 3.43 ppm with a two bond coupling constant to  $^{195}\text{Pt}$  of 96 Hz.

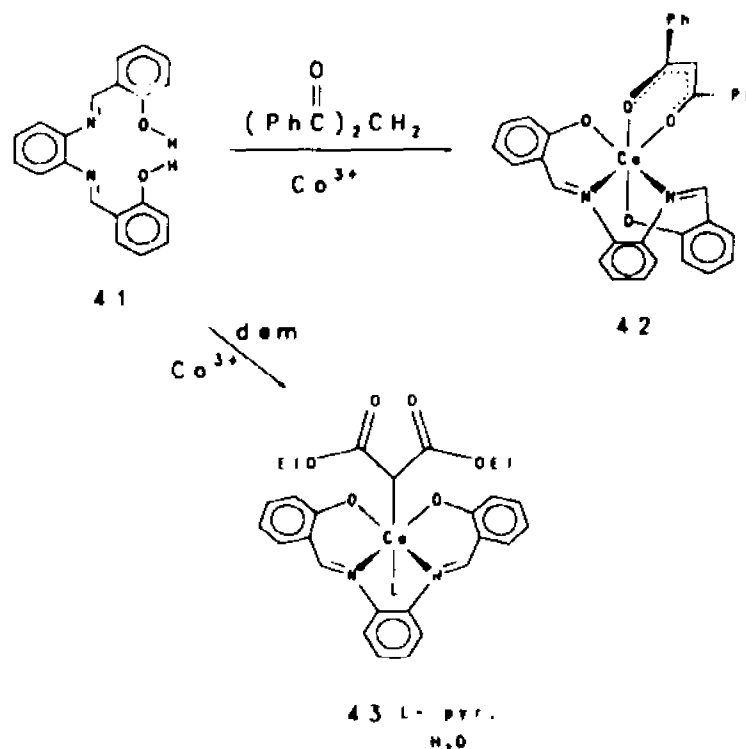


39  $\text{R} = \text{H}, \text{Et}$



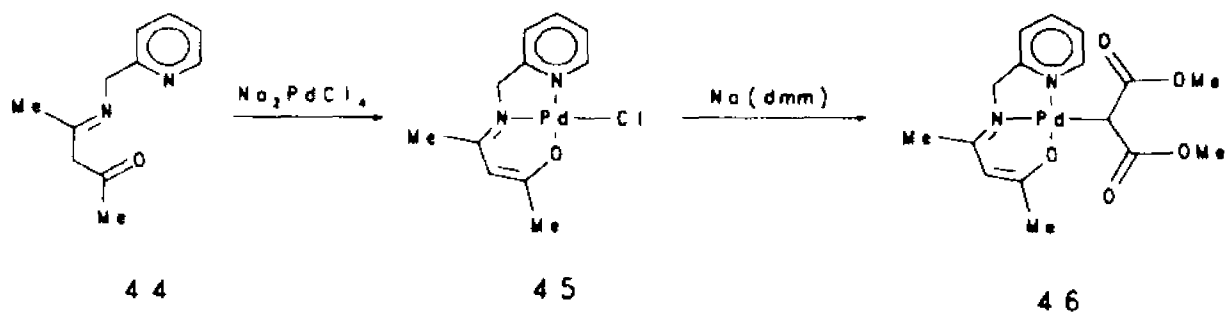
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The "rigid" tetradentate **41**<sup>92,93</sup> was used in an attempt to force C-bonding of  $\beta$ -dic ligands by capturing the equatorial positions of octahedral  $\text{Co}(\text{III})$  leaving only the axial positions available for unidentate ligands. However when 1,3-diphenyl-1,3-propanedione was used, **41** proved insufficiently rigid and the  $\beta$ -dik was bonded *via* a *O,O'*-chelate **42** (X-ray crystal structure determination). On the other hand, when diethyl malonate was used, the product **43** contained one C-bonded malonate as indicated by its IR (C=O frequencies greater than 1700  $\text{cm}^{-1}$ ) with pyridine or water



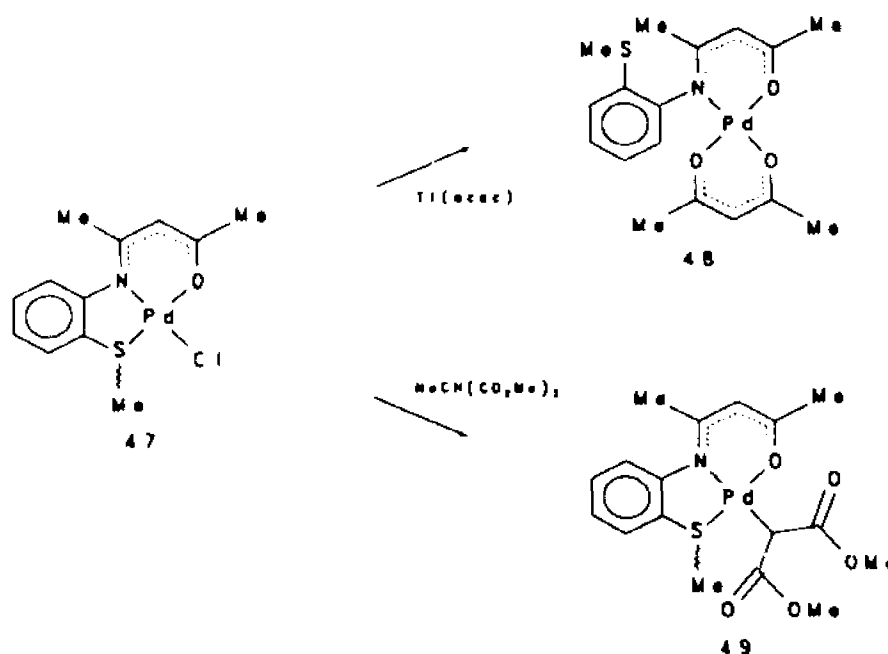
capping the other axial position.

Another strategy to force *C*-bonding of  $\beta$ -des ligands was reported<sup>94</sup> using the *O,N,N'*-tridentate **44**. By using Pd(II), which forms primarily four coordinate square planar complexes, only one coordination site would remain for the malonate to bind. Thus, reaction of **44** with  $\text{Na}_2\text{PdCl}_4$  in ethanol gave the chloro complex **45**, which subsequently was reacted with sodiummalonate in methanol to afford (31%) **46**. The analytical data of **46** were comparable to other *C*-bonded malonate complexes [IR ( $\text{C}=\text{O}$ )  $1714 \text{ cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  3.93 ( $\text{PdCH}$ );  $^{13}\text{C}$  NMR  $\delta$  28.2 ( $\text{PdC}$ )].

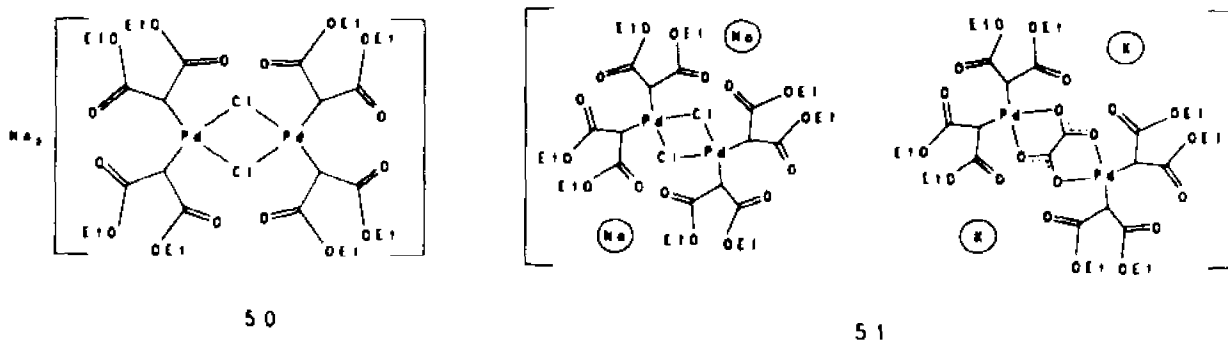




The same research group later reported<sup>95</sup> the synthesis of a new *O,N,S*-tridentate ligand in which the *S*-atom is labile thereby facilitating either *O,O'*-chelation or *C*-bonding. Reaction of the Pd(II) complex **47** with  $\text{Ti}(\text{acac})_3$  gave (17%) the *O,O'*-chelated complex **48** but reaction with sodiummalonate gave (48%) the *C*-bonded complex **49**, which had an IR  $\text{C}=\text{O}$  absorption at  $1718\text{ cm}^{-1}$ , a  $^1\text{H}$  NMR absorption at  $\delta\ 3.69$  ( $\text{PdCH}$ ) and a  $^{13}\text{C}$  NMR absorption at  $\delta\ 32.3$  ( $\text{PdC}$ ).

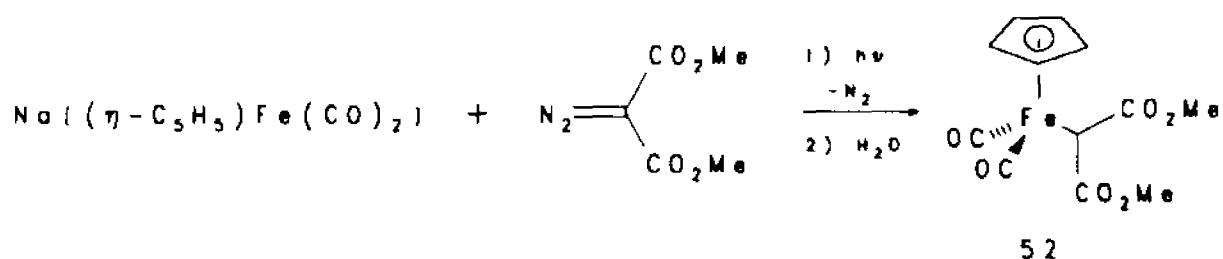


Reaction of diethyl malonate with  $\text{Na}_2\text{PdCl}_4$  in aqueous KOH gave two novel *C*-bonded products.<sup>96</sup> The major isolated (14%) product was dimer  $\text{Na}_2[\text{PdCl}(\text{dem})_2]_2$  (**50**) whose IR spectrum showed an absorption at  $1703\text{ cm}^{-1}$  (*C*-bonded). The minor

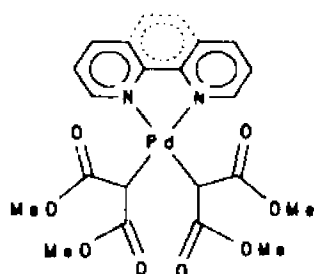


isolated (4.9%) product was the complex salt  $\text{Na}_2[\text{PdCl}(\text{dem})_2]_2\text{K}_2[\text{Pd}(\text{dem})_2]_2 \cdot (\text{C}_2\text{O}_4) \cdot 4\text{H}_2\text{O}$  (**51**) whose structure was determined by X-ray crystal data. The IR of **51** showed a  $\text{C}=\text{O}$  absorption at  $1710\text{ cm}^{-1}$ . The  $^1\text{H}$  NMR of both **50** and **51** did not show the  $\text{PdCH}$  protons due to limited solubility.

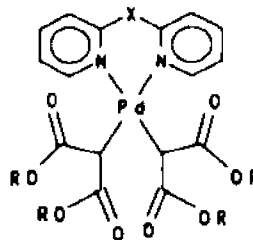
A non-typical synthesis of a *C*-malonatometallic complex has been reported<sup>97</sup> where  $\text{Na}[(\eta\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]$  was reacted with dimethyl diazomalonate under UV irradiation to give  $\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2(\text{dmm})$  (**52**) in 31% yield.



The first example of a complex which contained more than one *C*-bonded  $\beta$ -des ligand was reported by Newkome and Gupta in 1982.<sup>98</sup> Dichloro-2,2'-dipyridine-palladium(II) and dichloro-1,10-phenanthrolinepalladium(II) reacted with dimethyl malonate under extremely mild conditions ( $\text{K}_2\text{CO}_3$ , DMF,  $25^\circ\text{C}$ ) to give *cis* complexes **53**, which were stable in both air and solution. Interestingly, even with *cis* alkyl groups, these complexes did not undergo reductive elimination. The full account of the work reported<sup>99</sup> four new bis-malonato complexes which contained six- or seven-membered *N,N'*-chelates **54**, all of which were stable complexes; an X-ray crystal structure of **54d** proved that the malonates were *C*-bonded. In attempts to form the cyclometalated complex **55**, 1,3-dibromopropane was reacted with **54c** and **54d** and  $\text{K}_2\text{CO}_3$  in  $\text{CH}_3\text{CN}$ ; however, the only products obtained were the unsymmetrical bromo complexes **56**, whose structure was also proven by X-ray structure determination. A mechanism involving initial deprotonation of the metalated malonate, nucleophilic attack on dibromopropane, followed by  $\text{Br}^-$  displacement of the



53



- 54 a: X-CH<sub>2</sub>; R-Me  
 b: X-CH<sub>2</sub>CH<sub>2</sub>; R-Me  
 c: X- 1,3-dioxolane; R-Me  
 d: X- 1,3-dioxolane; R-Et

substituted malonate was proposed. However, this mechanism should give two complexes: one containing bromopropyl malonate (which was not reported) and **56**. The possibility of initial oxidative addition, followed by reductive elimination was not considered; exclusion of base could easily distinguish between the two. Although not investigated in depth, these cis Pd(II) complexes may possess significant anti-tumor activity because of the cis orientation of the diamino moiety and relative stability of the C-malonato palladium(II) bond. The <sup>1</sup>H NMR [PdCH - dipy: δ 4.12; phen: δ 4.25] substantiated C-bonding of the malonates.

Re-examination of the <sup>13</sup>C NMR data for **53** and **54c**<sup>98-100</sup> indicated errors in the assignments of the PdC carbons. The correct values are:

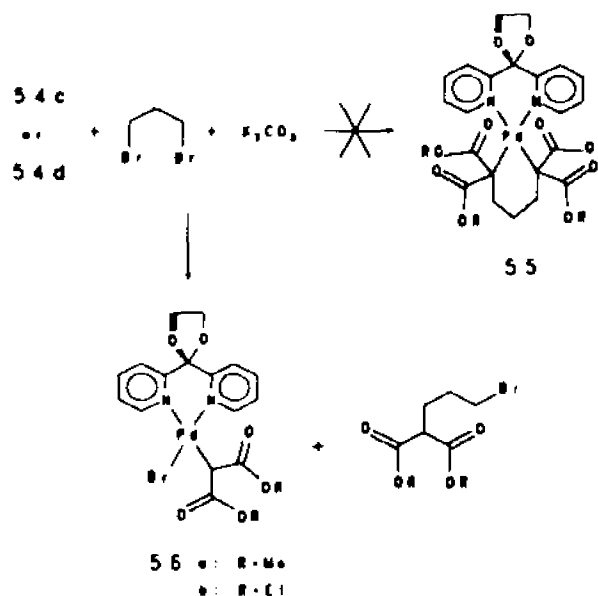
**53** (dipy) - δ 25.4

**53** (phen) - δ 25.6

**54c** (diox) - δ 24.3

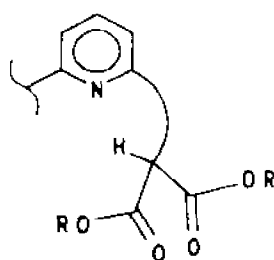
all of which are self-consistent and in the expected range of C-bonded malonate complexes.

A new approach to the synthesis of stable C-bonded β-des complexes has been taken by Newkome et al.<sup>100</sup> by incorporating both a dialkyl malonato moiety and a pyridine ring into one ligand **57** thereby taking advantage of added stabilization

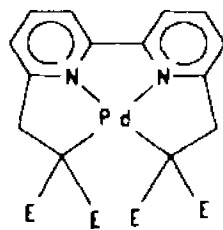
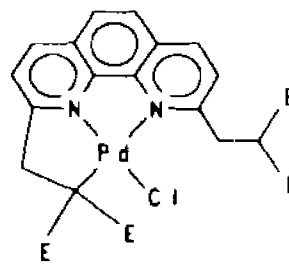


through *N,C*-chelation. Systems have been designed which facilitate both *cis* and *trans* carbon-metal bonds as well as fused bi- and tri-cyclic complexes. The first report of these ligand systems was of the fused tricyclic dipyrindine complex **58**<sup>101</sup> [IR (C=O) 1738  $\text{cm}^{-1}$ ], which was found to nick purified DNA and proposed to act similar to known intercalating anti-tumor platinum drugs [*cis*-Pt(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>].

The analogous 1,10-phenanthroline ligand cyclometalated on **one side only** to give **59**.<sup>100</sup> The X-ray crystal structure of **59** showed that the second carbanion was too far away from the metal center to allow Pd-C bond formation. The rationale for the difference between the dipyrindine and phenanthroline complexes was that the

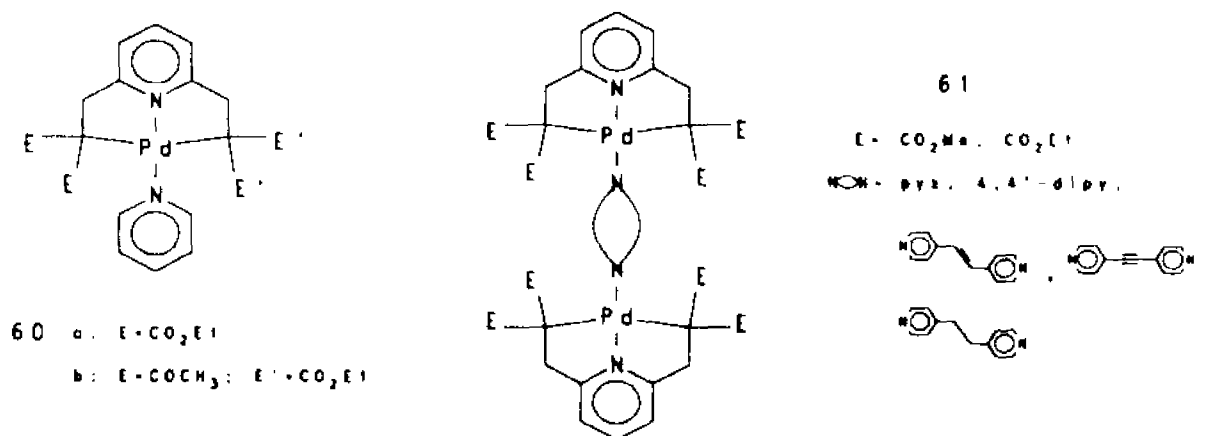


57

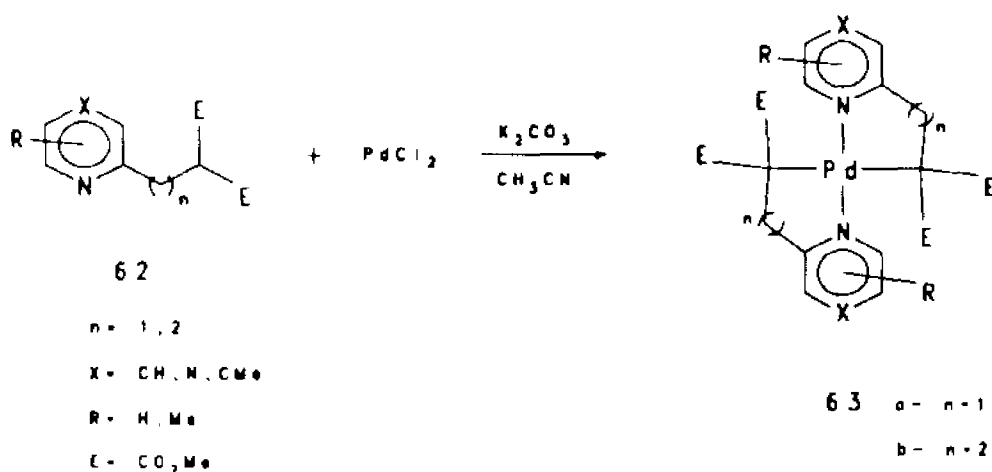
58  $\text{E} = \text{CO}_2\text{Et}$ 59  $\text{E} = \text{CO}_2\text{Me}, \text{CO}_2\text{Et}, \text{CO}_2\text{-i-Pr}$

phenanthroline backbone in **59** is not as flexible as the dipyridine bridge in **58**, which does allow bis-cyclometalation.

A related disubstituted pyridine ligand reacted with  $K_2PdCl_4$  to give the trans fused bicyclic complex **60**,<sup>102</sup> whose structure was proven by X-ray crystal structure data. This trans complex did **not** nick DNA lending support to the proposition that **58** acts similar to *cis*  $Pt(NH_3)_2Cl_2$ . Complex **60** has one non-chelated ligand (pyridine) which when replaced by a linear bidentate ligand (i.e. pyrazine, 4,4'-dipyridine) formed dinuclear complexes **61**.<sup>102</sup> An X-ray crystal structure of the pyrazine bridged dimer **61** proved the proposed structure.

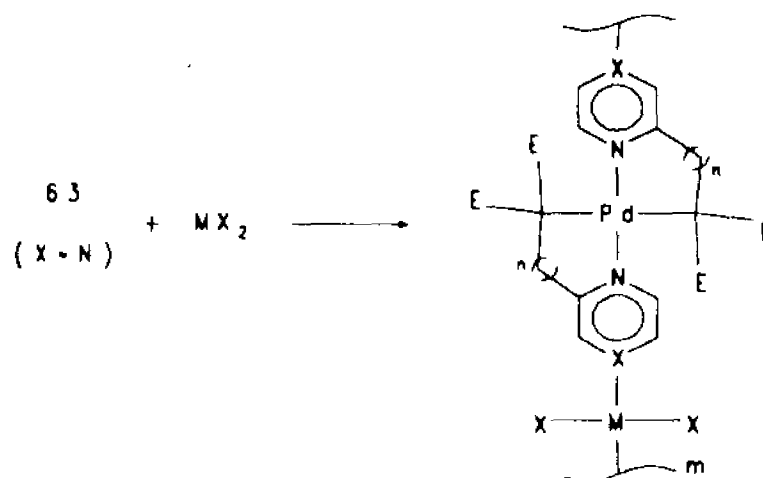


The simplest ligand in this series was the 1:1 pyridine(pyrazine):malonate ligand where the two moieties were joined by one<sup>103</sup> or two<sup>104</sup> methylene bridges (**62**).

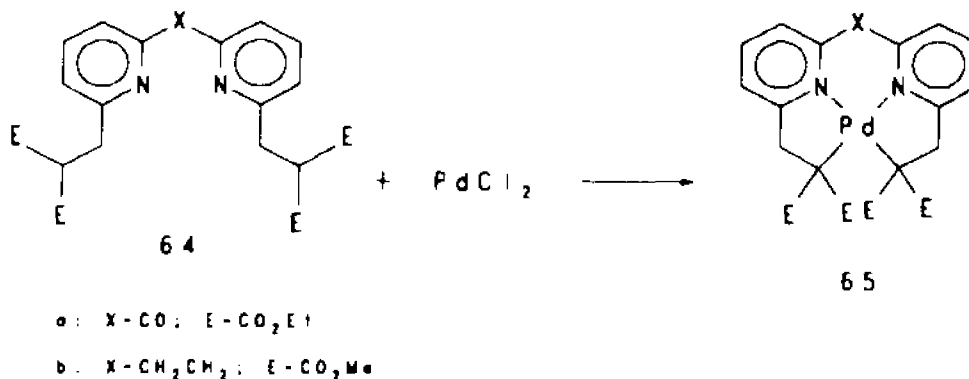


Reaction of **62** with  $\text{PdCl}_2$  in the presence of base gave the bis chelated trans complexes **63**, whose structures were proven by X-ray crystal structure data [ $\text{X} = \text{CH}$ ,  $\text{R} = \text{H}$ ,  $\text{E} = \text{CO}_2\text{Me}$ , ( $n = 1$ );<sup>103</sup> ( $n = 2$ )<sup>104</sup>].

The pyrazine complexes **63** are interesting in that mixed metal polymers with interesting electrochemical properties should be readily available through reaction with simple metal salts.

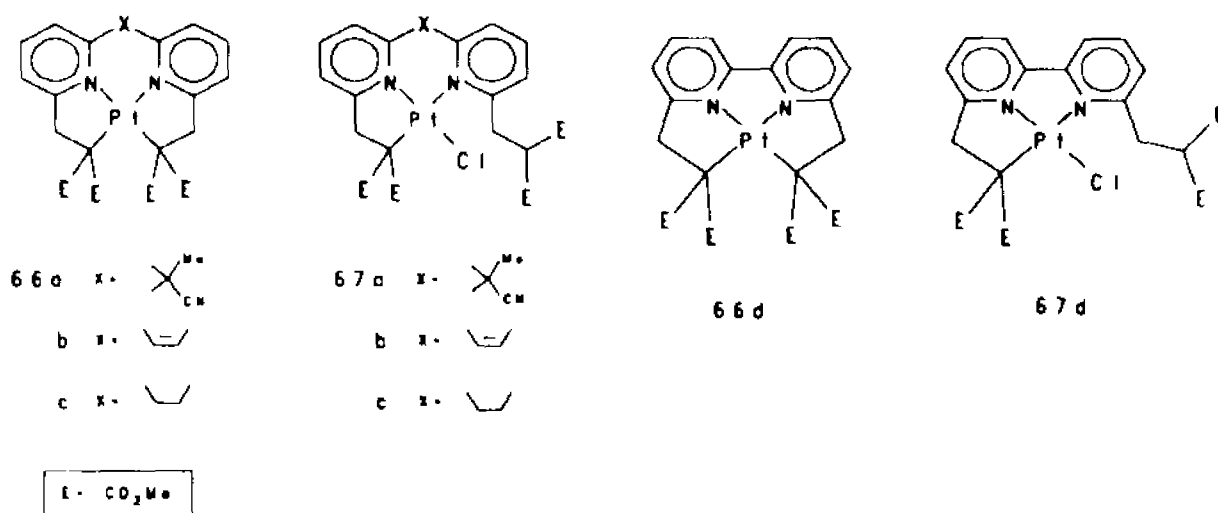


Expansion of the tricyclic [5.5.5] system **58** to [5.6.5]- and [5.7.5]-tricyclic systems was reported<sup>105</sup> by Newkome et al. in 1986. Thus, ligands **64** readily reacted with  $\text{PdCl}_2$  in the presence of base to give complexes **65** (X-ray of **65b**).



### C-Bonded Malonato Pt(II) Complexes

Prior to our initial work, there was only one example in the literature of an unsubstituted malonato ligand C-bonded to Pt(II) (**40**)<sup>20</sup> and the only Pt(IV) complexes, which incorporated a C-malonato ligand, were **36** in which the malonate acted as a terdentate ligand giving both C-bonded and O,O'-chelation.<sup>86</sup> In addition, we recently reported<sup>106</sup> the syntheses of several new cyclometalated complexes of Pt(II) (**66** and **67**) which are C,N,N',C'- and C,N,N'-chelates, respectively.



Our interest in platinum stems from the anti-tumor activity observed in cis diammine platinum complexes,<sup>107</sup> of which *cis*-diamminedichloroplatinum(II) ("cisplatin") is best known. The generally accepted mechanism for cisplatin's activity is initial preferential binding at the N(7) position of the guanine moiety of DNA,<sup>108</sup> replacing the chloride ligands, thereby forming intra-strand<sup>109</sup> cross-links which are the sites of nicking in the DNA.

Cisplatin is rather nonselective in that it binds both tumor and normal DNA. The lack of selectivity is generally associated with the lability of the Pt-Cl bond. It was rationalized that complexes in which the non-ammine ligands are not as labile as

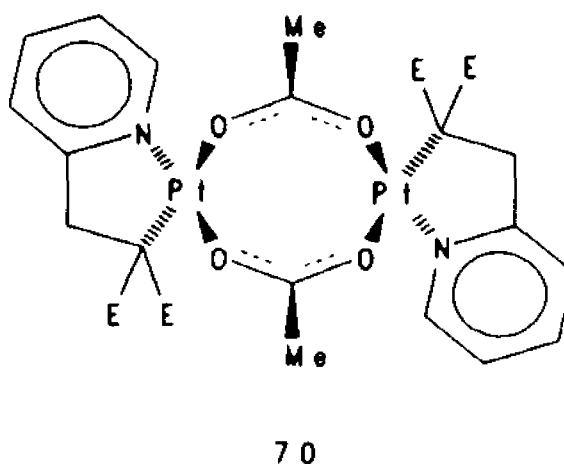
chloride but yet react with specific sites should lead to more selective anti-tumor activity than cisplatin. To this end, the cis complexes reported here, which contain Pt-C-malonato bonds, are prime candidates for anti-tumor activity, especially  $\text{Pt}(\text{phen})(\text{dmm})_2$  **71b** which, in addition to the possibility of Pt binding to DNA, also contains a phenanthroline ligand that can intercalate into DNA itself<sup>110</sup> thereby facilitating the complex's binding to DNA.

In order to compare the similarities and differences of palladium and platinum C-malonato complexes, the platinum analogs of the previously reported C-malonato complexes of two types: cyclometalated complexes **63** ( $\text{X} = \text{CH}$ ,  $\text{R} = \text{H}$ )<sup>103,104</sup> and the acyclic metalated complexes **53**<sup>99</sup> were prepared.

## Results

### Syntheses of C-Malonato Complexes

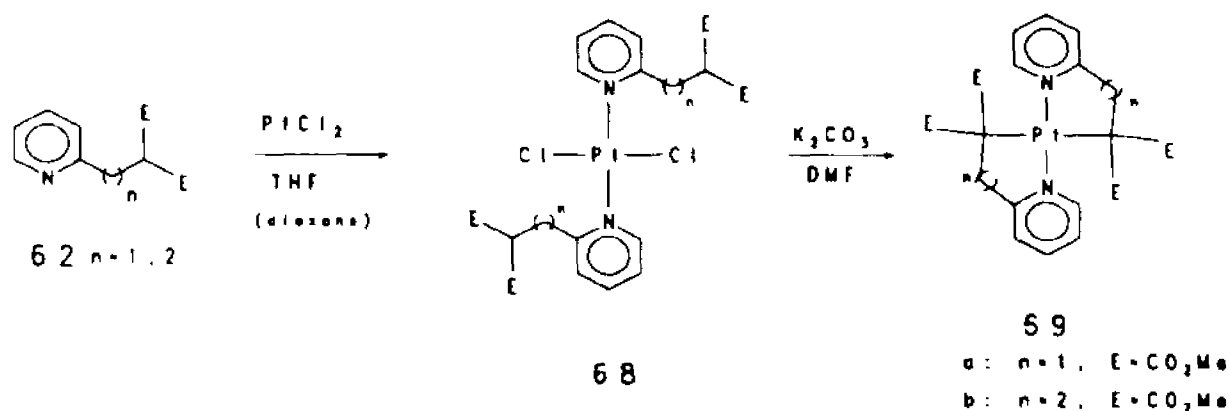
Because of the rapid aquation (hydrolysis) of platinum salts,<sup>111</sup> the initial 2:1 adducts **68** were elusive; alkaline aqueous conditions gave mixtures, presumably of both cis and trans isomers as well as aquated complexes. Despite these complex mixtures, the interesting acetate dimer **70**, whose structure was proven by X-ray crystal diffraction, was isolated from a reaction of  $\text{K}_2\text{PtCl}_4$  with **62** in an acetone/ $\text{H}_2\text{O}$  mixture utilizing KOH, as base. Since no acetate was added to the reaction, it was assumed that the commercially obtained  $\text{K}_2\text{PtCl}_4$  contained acetate as an impurity. Attempts to prepare **70** under controlled





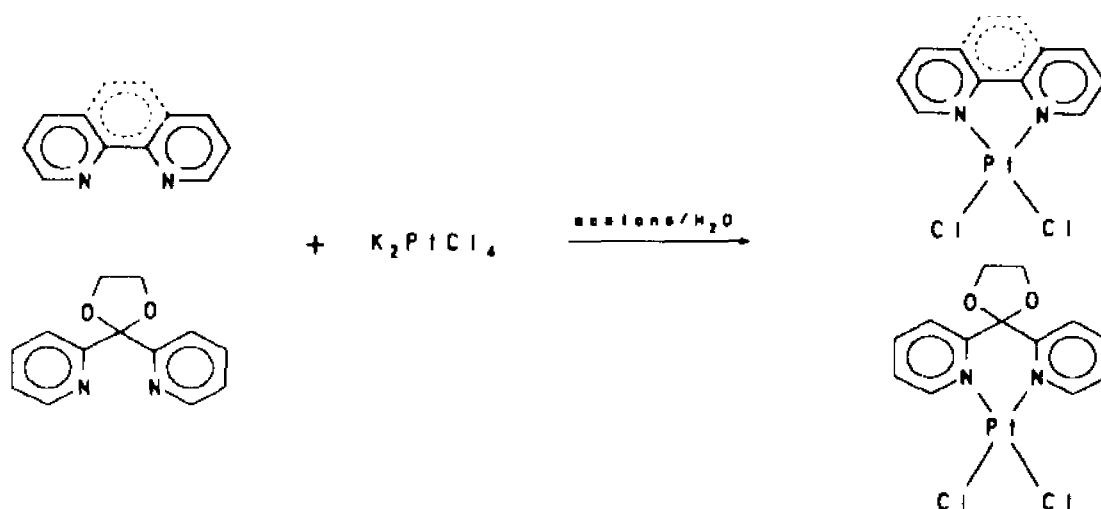
conditions as well as those to reproduce the initial preparation failed. Dimer **70** is the first example in which ligand **62** (or related ligands) was found to form a dimeric species; even in equimolar ratios, these ligands generally react to form 2:1 complexes.

Although reactions using  $K_2PtCl_4$  and the appropriate ligand in DMF or  $CH_3CN$  did not give the desired **68**, dichloroplatinum(II) did react with **62** in refluxing THF to give **68**, however, this reaction depended on the particular lot of  $PtCl_2$  used. In an effort to increase the solubility of  $PtCl_2$ , refluxing dioxane was used as solvent for this reaction with reproducible results being obtained, regardless of the lot of  $PtCl_2$  used.



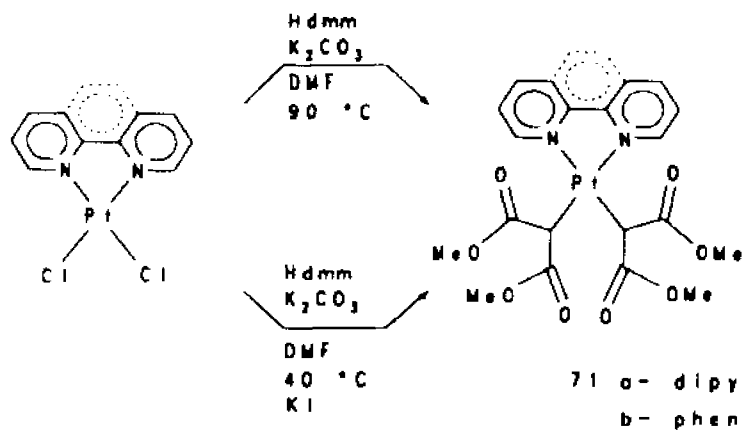
Initial attempts to make **69** using previously reported conditions ( $K_2CO_3$ , DMF, 25 °C) failed. The most obvious variable to change was the reaction temperature but even at 50 °C, no reaction occurred. Finally, at 90 °C, cyclometalation succeeded to give **69a** and **69b** in 84% and 19%, respectively. The low yield of **69b** was attributed to  $\beta$ -elimination of the cyclometalated complex at the elevated temperatures as shown by the appearance of vinyl absorptions in the  $^1H$  NMR spectrum of the crude mixture.

The adducts  $Pt(phen)Cl_2$ ,  $Pt(dipy)Cl_2$ , and  $Pt(diox)Cl_2$  (diox = 1,1-bis(2-pyridyl)-1,3-dioxolane) were prepared by a modified procedure of Rosenblatt and Schleede<sup>112</sup> where acetone solutions of the ligands were added to an aqueous solution of  $K_2PtCl_4$



from which the product precipitated. Elevated temperatures (90 °C) were again required for metalation; **71a** and **71b** were obtained in 78% and 76%, respectively. Under these strenuous conditions, it was apparent that dimethyl malonate had self-condensed to give a small amount of a thick oil which was easily removed by chromatography. Pt(diox)Cl<sub>2</sub> did not react under any of our conditions.

Presumably the metalations require high temperatures due to the relative insolubility of the Pt(L)Cl<sub>2</sub> adducts in DMF. To circumvent this problem, KI was added to the metalation reactions to generate Pt(L)I<sub>2</sub> in situ which, if not more soluble, would certainly be more reactive. An initial test reaction at 25 °C using Pt(phen)Cl<sub>2</sub>, Hdmm,



$\text{K}_2\text{CO}_3$ , and KI in DMF indeed gave (63%)  $\text{Pt}(\text{phen})(\text{dmm})_2$  **71b** along with some mono- and un-substituted products; raising the temperature to 40 °C improved the yield of **71b** to 80%. The complex  $\text{Pt}(\text{dipy})\text{Cl}_2$ , under identical conditions, gave (74%)  $\text{Pt}(\text{dipy})(\text{dmm})_2$  (**71b**); however,  $\text{Pt}(\text{diox})\text{Cl}_2$  gave a complex mixture from which no pure complexes were isolable. Unfortunately, attempts using KI to effect cyclometalation on **68** at lower temperatures ( $\approx 40$  °C) also failed.

### Reactivity of Pt(II) C-Malonato Complexes

Simple alkyl organoplatinum(II) complexes are known to react with numerous organic substrates such as alkyl and acyl halides, as well as olefins<sup>113</sup> (Figure 4); however,  $\text{Pt}(\text{phen})(\text{dmm})_2$  (**71b**) failed to react with methyl vinyl ketone, acetyl chloride or benzoyl chloride, in which each returned the unchanged complex. Reaction of **71b** with methyl iodide gave a complex mixture which included  $\text{Pt}(\text{phen})\text{I}_2$

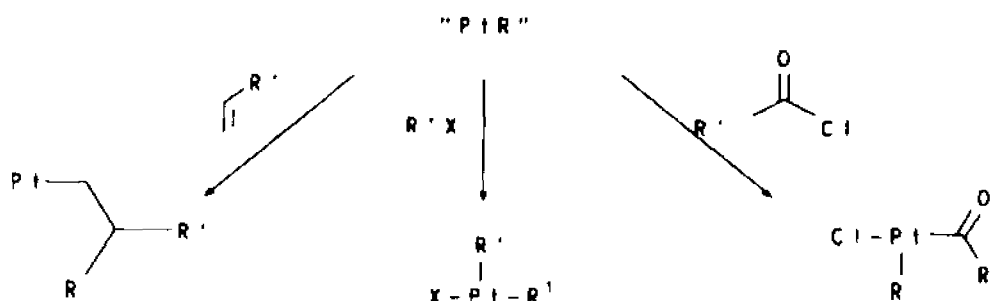


Figure 4. Reactions of Organoplatinum Complexes.

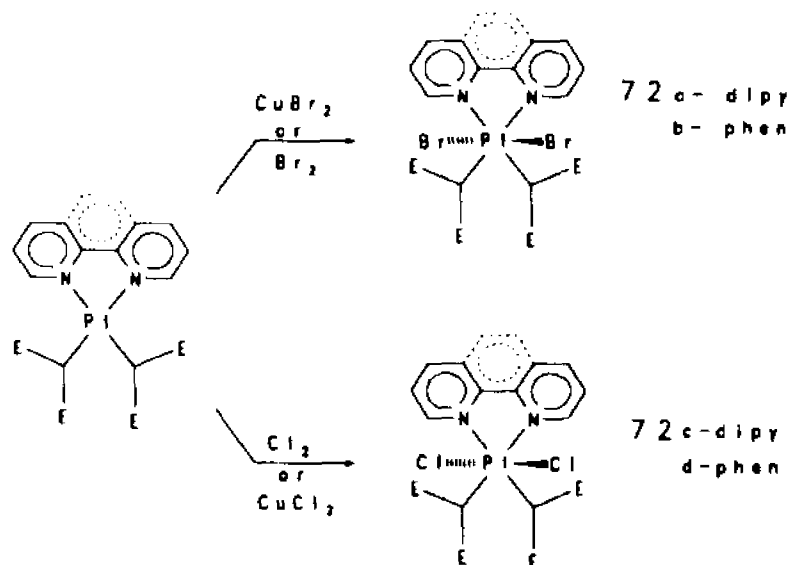
(probably by two consecutive oxidative addition/reductive elimination sequences whereby dimethyl methylmalonate should also be formed but was not investigated).



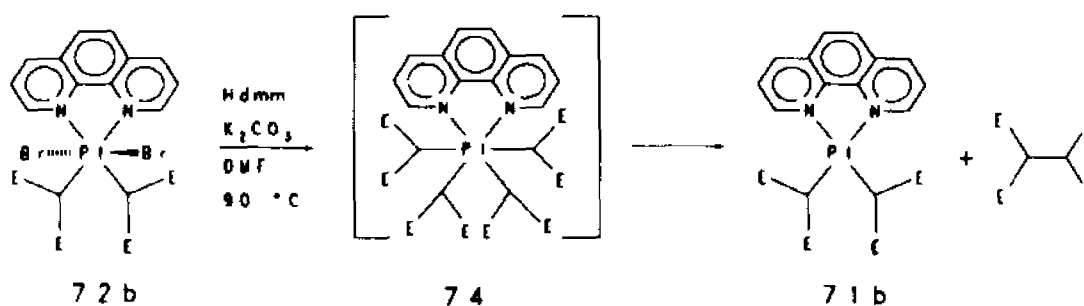
reagent - acetyl chloride,  
benzoyl chloride,  
methyl vinyl ketone

Organoplatinum(II) complexes are also known to undergo ligand-ligand exchange,<sup>113</sup> for example the transfer of a C-malonato ligand. However, attempts to react **71b** with  $\text{Pt(phen)Cl}_2$  to obtain  $\text{Pt(phen)(dmm)Cl}$  gave only starting complexes.

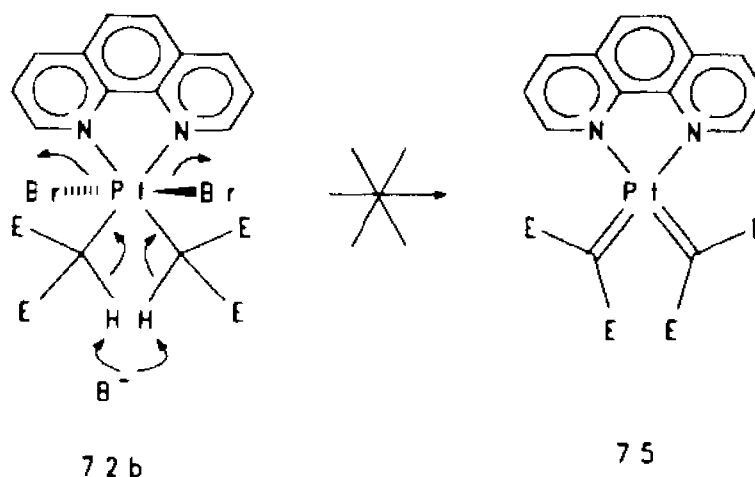
Oxidation of organoplatinum(II) complexes can be accomplished using  $\text{X}_2$ , and accordingly, when  $\text{Br}_2$  was added to either  $\text{Pt(dipy)(dmm)}_2$  (**71a**) or  $\text{Pt(phen)(dmm)}_2$  (**71b**), the corresponding  $\text{Pt(dipy)(dmm)}_2\text{Br}_2$  (**72a**) or  $\text{Pt(phen)(dmm)}_2\text{Br}_2$  (**72b**), respectively, was immediately formed, both in 98% yield. Predominant trans addition occurred<sup>114</sup> as determined by symmetry in the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of the Pt(IV) complexes. Use of  $\text{Cl}_2$  also effected oxidation of **71a** and **71b**; lower yields were realized probably due to oxidation of the ligand. Interestingly, the oxidation could be conducted using  $\text{CuCl}_2$  (**72c**, **72d**, and **73**) or  $\text{CuBr}_2$  (**72a** and **72b**) as the oxidant, in general the yields were lower (70-90%) than with  $\text{Br}_2$  but higher than with  $\text{Cl}_2$ . Although  $\text{CuX}_2$  reacts with organometallic complexes by cleaving the C-metal bond,<sup>115</sup> Terheijden has recently reported<sup>116</sup> the oxidation of platinum(II) complexes with  $\text{CuX}_2$  and reported lower yields than with  $\text{X}_2$ . One by-product isolated from the reaction of  $\text{Pt(phen)(dmm)}_2$  (**71b**) with  $\text{CuCl}_2$ , was the cis addition product giving (5%) the



unsymmetric *cis*-(dichloro)-*bis*-(dimethyl malonato-C)-1,10-phenanthrolineplatinum(IV) (**73**). Pt(dipy)(dmm)<sub>2</sub> (**71a**) gave much cleaner reactions with CuX<sub>2</sub> than did Pt(phen)(dmm)<sub>2</sub> (**71b**).



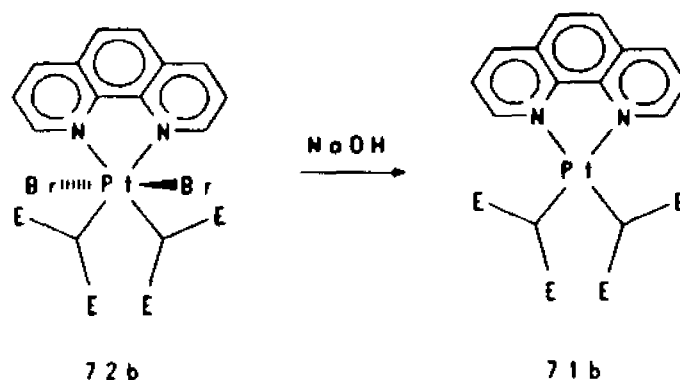
Attempts to react **72b** with excess Hdmm to form the Pt(IV) complex Pt(phen)(dmm)<sub>4</sub> (**74**), which contains four C-malonato ligands, gave instead the reduced product Pt(phen)(dmm)<sub>2</sub> (**71b**). Complex **74** may have formed in the reaction but then underwent reductive elimination to give the reduced complex **71b**. An



alternative explanation is that potassiummalonate attacked one of the bromides with concomitant reduction of platinum.

The Pt(IV) complex **72b** possesses two acidic protons and upon treatment with base and elimination of two equivalents of HBr, the di-carbene complex **75** (or its

polynuclear equivalent) was expected to form; however, treatment of **72b** with NaOH gave (25%) Pt(phen)(dmm)<sub>2</sub> (**71b**) probably with loss of HOBr and Br<sup>-</sup>. The other possible mechanism, which could explain this product, is reductive elimination of Br<sub>2</sub>; however, this is not likely due to the greater propensity for alkyl-alkyl elimination as opposed to Br-Br elimination. After work-up, the mixture rapidly turned dark green perhaps an indication of the decomposing intermediate **75**.



### Characterization of Platinum C-Malonato Complexes

Table I contains important analytical data for various palladium(II) and platinum(II) C-malonato complexes for comparison purposes.

One of the most important features about the <sup>1</sup>H and <sup>13</sup>C NMR spectra of platinum complexes is the fact that, of the six stable isotopes of platinum, only one isotope, namely <sup>195</sup>Pt, has a nuclear spin (1/2). It has a relatively high natural abundance (33.8%) and gyromagnetic ratio ( $\gamma = 5.7412$ ) allowing the <sup>195</sup>Pt-H and <sup>195</sup>Pt-C couplings to be easily observed. Because <sup>195</sup>Pt does not have a natural abundance of 100%, a singlet in the <sup>1</sup>H NMR spectrum appears as a 1:4:1 triplet: a singlet due to the molecules which have <sup>194</sup>Pt with no spin (66.2%) and a doublet (usually called satellites) due to molecules containing <sup>195</sup>Pt (33.8%) (see Figure 5).

As with H-H or C-H coupling constants, the <sup>195</sup>Pt-H and <sup>195</sup>Pt-C coupling constants










non-spin Pt			
$^{195}\text{Pt}$			
"Pt"			

Figure 5. Appearance of a Singlet, a Doublet, and a Triplet Coupled to Platinum.

decrease in magnitude as the distance (number of bonds) between the nuclei increases. Thus for a malonato ligand, the magnitude of the  $^{195}\text{Pt}-\text{C}$  and  $^{195}\text{Pt}-\text{CH}$  coupling constants can be used to ascertain if  $O,O'$ -chelation or  $\text{C}$ -bonding occurred.

The coupling constants  $J_{\text{PtX}}$  can be either positive or negative. However, in this work, only the absolute values of the coupling constants are reported.

Table 1. Selected analytical data for C-bonded  $\beta$ -dicarbonyls.

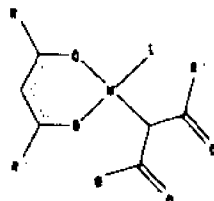
Compound	M	R	R'	L	$^1\text{H}$ NMR [MCH( $^2J_{\text{PdH}}$ )]	$^{13}\text{C}$ NMR [MC( $^1J_{\text{PdC}}$ )]	IR [C-bonded C=O, $\text{cm}^{-1}$ ]
	Pd <sup>a</sup>	Me	Me	PPh <sub>3</sub>	3.54	51.1	1670s, 1640s
	Pd <sup>b</sup>	Me	Me	PEt <sub>3</sub>	3.53	--	1683vs, 1650vs 1568vs, 1515vs
	Pd <sup>b</sup>	Me	Me	PMePh <sub>2</sub>	3.72	--	--
	Pd <sup>b</sup>	Me	Me	PPhMe <sub>2</sub>	3.55	--	--
	Pd <sup>a</sup>	Me	Me	PCy <sub>3</sub>	3.44	--	1675s, 1665m
	Pd <sup>b</sup>	Ph	Me	PPh <sub>3</sub>	4.38	47.8(cis)	1653vs, 1558vs 1517vs
	Pd <sup>b</sup>	CF <sub>3</sub>	Me	PPh <sub>3</sub>	3.91(cis) 3.98(trans)	43.4 43.9	1715vs, 1665vs 1615vs, 1523vs
	Pd <sup>b</sup>	thienyl	CF <sub>3</sub>	PPh <sub>3</sub>	4.34, 4.41 cis/trans)	--	--
	Pt <sup>c,d</sup>	OMe	OMe	PPh <sub>3</sub>	3.72(96)	--	1740, 1715
	Pt <sup>c,d</sup>	OMe	Me	PPh <sub>3</sub>	3.89(105)	--	1735, 1715
	Pt <sup>c,d</sup>	OEt	Me	PPh <sub>3</sub>	3.85(101)	--	1710
	Pt <sup>a</sup>	Me	Me	PPh <sub>3</sub>	4.04(110)	41.3	1685s, 1650s
	Pt <sup>a</sup>	Me	Me	PCy <sub>3</sub>	3.99	--	1645s
	Pt <sup>e</sup>	Me	Me	pyr	5.05(129)	41.7(619)	1700s, 1655m



Table I. Selected analytical data for C-bonded  $\beta$ -dicarbonyls (continued).

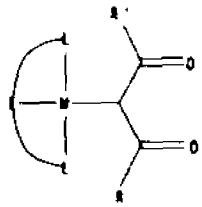
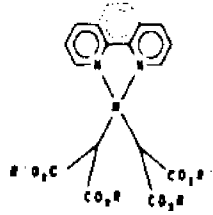
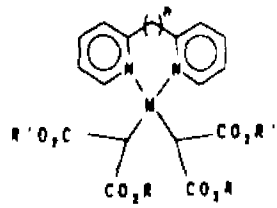
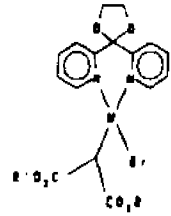
Compound	M	R	R'	L	$^1\text{H}$ NMR [MCH( $^2J_{\text{PdH}}$ )]	$^{13}\text{C}$ NMR [MC( $^1J_{\text{PC}}$ )]	IR [C-bonded C=O, $\text{cm}^{-1}$ ]
	Pd <sup>f</sup>	OMe	OMe	N,N,O	3.93	28.2	1714s
	Pd <sup>g</sup>	OMe	OMe	O,N,S	3.69	32.3	1718
	Pd <sup>h</sup>	OMe	OMe	dipy	4.12	25.0 <sup>a</sup>	--
	Pd <sup>h</sup>	OMe	OMe	phen	4.25	25.3 <sup>i</sup>	--
	Pt	OMe	OMe	phen	4.81(130)	18.8(634)	1725
	Pt	OMe	OMe	dipy	4.68(129)	19.7(635)	1744,1721
	Pd <sup>j</sup>	OMe	OMe	n=2	3.67	52.0 <sup>k</sup>	--
	Pd <sup>j</sup>	OMe	OMe	n=1	3.75	--	1708
	Pd <sup>j</sup>	OMe	OMe	diox	4.39	--	1695
	Pd <sup>j</sup>	OEt	OEt	diox	4.17	--	1705

Table I. Selected analytical data for C-bonded  $\beta$ -dicarbonyls (continued).

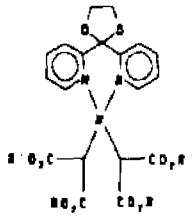
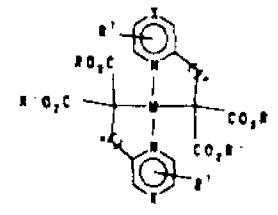
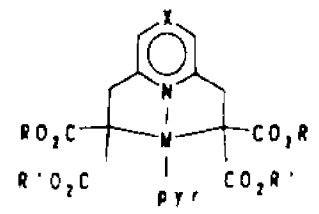
Compound	M	R	R'	L	$^1\text{H}$ NMR [MCH( $^2J_{\text{PH}}$ )]	$^{13}\text{C}$ NMR [MC( $^1J_{\text{PC}}$ )]	IR [C-bonded C=O, $\text{cm}^{-1}$ ]
	Pd <sup>II</sup>	OMe	OMe	diox	3.85	52.3 <sup>k</sup>	1700
	Pd <sup>II</sup>	OEt	OEt	diox	3.87	--	1690
	Pd <sup>I</sup>	OMe	OMe	n=1; R <sup>I</sup> =H; X=CH	--	53.6	1670
	Pd <sup>III</sup>	OMe	OMe	n=2; R <sup>I</sup> =H; X=CH	--	45.6	--
	Pd <sup>I</sup>	OMe	OMe	n=1; R <sup>I</sup> =4-Me; X=CH	--	53.1	1680
	Pd <sup>I</sup>	OMe	OMe	n=1; R <sup>I</sup> =5-Me; X=CH	--	52.9	1730-1670b
	Pd <sup>I</sup>	OMe	OMe	n=1; R <sup>I</sup> =H; X=N	--	54.6	1700-1645b
	Pd <sup>I</sup>	OMe	OMe	n=1; R <sup>I</sup> =3-Me; X=N	--	52.6	1710-1680b
	Pd <sup>I</sup>	OMe	OMe	n=1; R <sup>I</sup> =5-Me; X=N	--	54.3	1710-1670b
	Pt	OMe	OMe	n=1; R <sup>I</sup> =H; X=CH	--	49.3(453)	1686vs
	Pt	OMe	OMe	n=2; R <sup>I</sup> =H; X=CH	--	41.4(448)	1690s
	Pd <sup>n</sup>	OMe	OMe	X=CH	--	51.0	--
	Pd <sup>n</sup>	OMe	OMe	X=N	--	51.6	--

Table I. Selected analytical data for C-bonded  $\beta$ -dicarbonyls (continued).

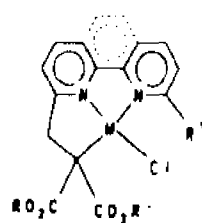
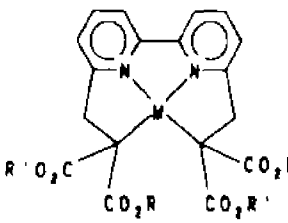
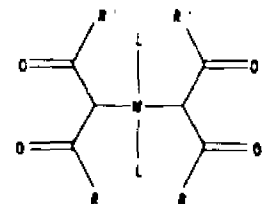
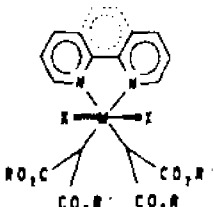
Compound	M	R	R'	L	$^1\text{H}$ NMR [MCH( $^2J_{\text{PdH}}$ )]	$^{13}\text{C}$ NMR [MC( $^1J_{\text{PdC}}$ )]	IR [C-bonded C=O, $\text{cm}^{-1}$ ]
	Pd <sup>n</sup>	OEt	OEt	dipy; R <sup>1</sup> =H	--	46.4	1700
	Pd <sup>n</sup>	OEt	OEt	dipy; R <sup>1</sup> =Me	--	46.7	--
	Pd <sup>n</sup>	OEt	OEt	dipy; R <sup>1</sup> =CH <sub>2</sub> dem	--	52.9	1728
	Pd <sup>n</sup>	OMe	OMe	phen; R <sup>1</sup> =CH <sub>2</sub> dem	--	52.7	--
	Pd <sup>n</sup>	OEt	OEt	----	47.4	--	
	Pt <sup>e</sup>	Me	Me	pyr	4.29(102)	60.3(369)	1650vs,1610s

Table I. Selected analytical data for C-bonded  $\beta$ -dicarbonyls (continued).

Compound	M	R	R'	L	$^1\text{H}$ NMR [MCH( $^2J_{\text{PH}}$ )]	$^{13}\text{C}$ NMR [MC( $^1J_{\text{PC}}$ )]	IR [C-bonded C=O, $\text{cm}^{-1}$ ]
	Pt	OMe	OMe	phen; X=Br	5.04(90)	21.1(560)	1746s
	Pt	OMe	OMe	dipy; X=Br	4.94(90)	21.0(557)	1744
	Pt	OMe	OMe	phen; X=Cl	5.09(89)	23.9(561)	1744
	Pt	OMe	OMe	dipy; X=Cl	4.93(89)	21.0(556)	1742

a) Reference 14. b) Reference 18. c) Reference 20. d) The *O,O'*-chelate is acac. e) Reference 15. f) Reference 94. g) Reference 95. h) Reference 98. i) Literature values were incorrectly reported. j) Reference 99. k) Literature values are probably incorrect. l) Reference 103. m) Reference 104. n) Reference 100

### Proton NMR Spectroscopy of the Pt(II) Complexes

Upon complexation to form the  $\text{Pt}(\text{L})_n\text{Cl}_2$  adducts, the main change in the  $^1\text{H}$  NMR spectra relative to the ligands is a downfield shift for the aromatic proton [H-2(6)] nearest the ligating nitrogen atom (H-6 for pyridine/dipyridine and H-2 for phenanthroline). This shift is electronic in nature due to the electron-withdrawing effect of the Pt on the ring.<sup>117</sup> As observed in other pyridine Pt(II) complexes,<sup>118</sup> this same proton is also coupled to  $^{195}\text{Pt}$  with a coupling constant ( $^3J$ ) range of 28.8-46.6 Hz. The  $N,N'$ -chelated complexes have larger coupling constants (L = diox: 46.6 Hz; phen: 41.3 Hz; dipy: 40.4 Hz) than the trans complexes **68a** and **68b** (28.8 and 30.8 Hz, respectively) which probably reflects the relative "trans effects" of chloride versus nitrogen. The other ring protons are probably also coupled to  $^{195}\text{Pt}$  but at 80 MHz could not be observed.

In the spectrum of the complexes containing Pt-C-malonato bonds, the most important features are the malonato *CH* chemical shifts and  $^2J$   $^{195}\text{Pt}$ -H coupling constants. Upon metalation, the remaining proton on malonate shifted downfield relative to unsubstituted malonate (3.39 ppm) with a range of 4.68-5.38 ppm. Although bordering the vinyl region expected for a  $O,O'$ -chelate, the effect is rather a *downfield* shift resulting from increased C-substitution.

The data which best supported C-bonding of the malonate ligand are the  $\text{PtCH}$  coupling constants which, for the complexes reported here, are only possible in the  $N,N'$ -chelates. For the complexes reported here, the range for  $^2J_{\text{PtH}}$  is 125.9-129.9 Hz. This coupling constant is too large for an  $O,O'$ -chelate having a four-bond coupling constant. Interestingly, the  $^2J_{\text{PtH}}$  coupling constant in various methyl platinum complexes ranges from -50 to -85 Hz,<sup>113</sup> much lower than those observed here. The only other Pt(II)-C-malonato complex reported<sup>20</sup> was **40** which had a  $^2J_{\text{PtH}}$  coupling

constant of 96 Hz.

Although complex **69a** showed symmetry in its NMR spectra, complex **69b** was clearly less symmetric in that two different methoxy protons were seen in the  $^1\text{H}$  NMR spectrum with one having a large upfield shift ( $\delta$  2.83). Also, in the  $^{13}\text{C}$  NMR spectrum, in addition to two methoxy carbons ( $\delta$  49.7, 50.6), two carbonyl resonances were observed ( $\delta$  174.5, 176.5). This will be discussed further in the X-ray discussion.

Comparing the  $\text{Pt}(\text{L})_n\text{Cl}_2$  adducts to the *C*-malonato complexes (**69** and **71**), the *N,N'*-chelates again showed a downfield shift of the ring protons nearest nitrogen [H-2(6)]: for  $\text{Pt}(\text{phen})(\text{dmm})_2$  and for  $\text{Pt}(\text{dipy})(\text{dmm})_2$   $\Delta\delta$  were 0.73 and 0.49 ppm, respectively. However in the *C,N*-chelates, complex **69a**'s H-6 shifted downfield only 0.09 ppm and complex **69b**'s H-6 shifted *upfield* by 0.18 ppm. This is probably due to increased steric interaction in the cyclometalated complexes between H-6 and the ester moieties of the trans ligand which is absent in the adducts. (A crude X-ray crystal structure determination of adduct **68a** showed that the pyridine ligands are perpendicular to the coordination plane with no non-bonded intramolecular contacts.)

The ring  $^3J_{\text{PtH}}$  coupling constants for these same protons are decreased in the *N,N'*-chelates ( $^3J_{\text{PtH}} = 25.6$  Hz for both **71a** and **71b**; an average decrease of 15.2 Hz) but *increased* in the *C,N*-chelates ( $^3J_{\text{PtH}} = 36.8$  and 40.4 Hz for **69a** and **69b**, respectively; an average increase of 8.8 Hz). Also worth noting is a small five-bond coupling of the methoxy protons to  $^{195}\text{Pt}$  of 3.0 Hz for **71a** and 3.4 Hz for **71b**.

Although in most of the Pt complexes'  $^1\text{H}$  NMR spectra the shifts are similar to the corresponding Pd complexes, a couple of shifts are significantly different. For the *N,N'*-chelates, the PtCH shifts are downfield of the PdCH shifts [ $\text{M}(\text{dipy})(\text{dmm})_2$ : Pd = 4.12, Pt = 4.68 ppm;  $\text{M}(\text{phen})(\text{dmm})_2$ : Pd = 4.25, Pt = 4.81 ppm; an average

downfield shift of 0.56 ppm]. Also the Pt complexes' H-2(6) protons are shifted downfield relative to the analogous Pd complexes [M(dipy)(dmm)<sub>2</sub>: Pd = 9.74, Pt = 10.09 ppm; M(phen)(dmm)<sub>2</sub>: Pd = 10.07, Pt = 10.44 ppm; complex **69a**: Pd = 9.06, Pt = 9.25 ppm; an average downfield shift of 0.30 ppm]. In one example, Pt(diox)Cl<sub>2</sub>, the Pt complex's H-6 is shifted *upfield* from the Pd complex: Pd(diox)Cl<sub>2</sub>: H-6 = 9.42 ppm;<sup>119</sup> Pt(diox)Cl<sub>2</sub>: H-6 = 9.37 ppm.

Complete <sup>1</sup>H NMR spectral data for the Pt(II) complexes are presented in Table II.

Table II. Proton NMR spectral data for the Pt(II) complexes and comparison with the Pd(II) analogs.<sup>a</sup>

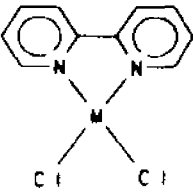
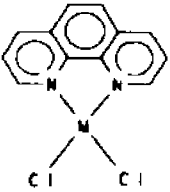
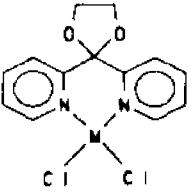
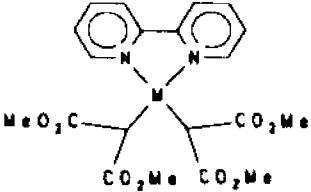
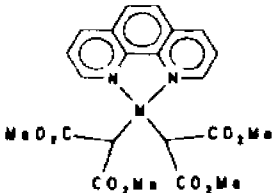
Compound	Assignment	Pd(II)	Pt(II)	$ ^aJ_{\text{PtH}} $
	5-pyrH	b	7.83 <sup>c</sup>	$^3J_{\text{PtH}} = 40.4 \text{ Hz}$
	3-pyrH	b	8.34 <sup>c</sup>	
	4-pyrH	b	8.48-8.71 <sup>c</sup>	
	6-pyrH	b	9.50 <sup>c</sup>	
	3-phenH	b	8.17 <sup>c</sup>	$^3J_{\text{PtH}} = 41.3 \text{ Hz}$
	5-phenH	b	8.29 <sup>c</sup>	
	4-phenH	b	9.04 <sup>c</sup>	
	2-phenH	b	9.71 <sup>c</sup>	
	CH <sub>2</sub>	4.34-4.45 <sup>d</sup>	4.25-4.45	$^3J_{\text{PtH}} = 46.6 \text{ Hz}$
	5-pyrH	7.31 <sup>d</sup>	7.40	
	3,4-pyrH	7.84-7.94 <sup>d</sup>	7.79-8.04	
	6-pyrH	9.42 <sup>d</sup>	9.37	
	CH <sub>3</sub>	3.62 <sup>c</sup>	3.62	$^5J_{\text{PtH}} = 3.0 \text{ Hz}$
	CH	4.12 <sup>c</sup>	4.68	$^2J_{\text{PtH}} = 129.4 \text{ Hz}$
	5-pyrH	7.56 <sup>c</sup>	7.61	$^3J_{\text{PtH}} = 25.6 \text{ Hz}$
	3-pyrH	8.00 <sup>c</sup>	7.99-8.19	
	4-pyrH	8.10 <sup>c</sup>	7.99-8.19	
	6-pyrH	9.74 <sup>c</sup>	10.09	
	CH <sub>3</sub>	3.66 <sup>c</sup>	3.64	$^5J_{\text{PtH}} = 3.4 \text{ Hz}$
	CH	4.25 <sup>c</sup>	4.81	$^2J_{\text{PtH}} = 129.9 \text{ Hz}$
	5-phenH	7.86 <sup>c</sup>	7.89	$^3J_{\text{PtH}} = 25.6 \text{ Hz}$
	3-phenH	7.87 <sup>c</sup>	7.93	
	4-phenH	8.41 <sup>c</sup>	8.53	
	2-phenH	10.07 <sup>c</sup>	10.44	



Table II. Proton NMR spectral data for the Pt(II) complexes and comparison with the Pd(II) analogs (continued).

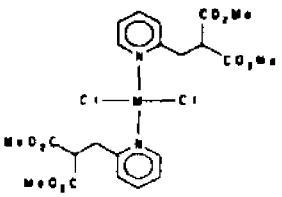
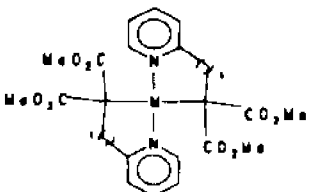
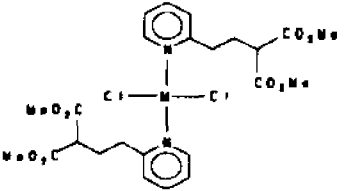
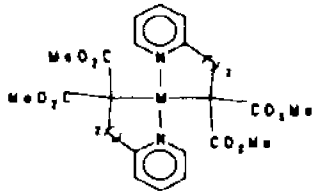
Compound	Assignment	Pd(II)	Pt(II)	$ ^nJ_{\text{PtH}} $
	$\text{CH}_3$	b	3.80 <sup>f</sup>	$^3J_{\text{PtH}} = 30.8 \text{ Hz}$
	$\text{CH}_2$	b	4.35 <sup>f</sup>	
	$\text{CH}$	b	5.35 <sup>f</sup>	
	5-pyrH	b	7.14-7.32 <sup>f</sup>	
	3-pyrH	b	7.44-7.76 <sup>f</sup>	
	4-pyrH	b	7.44-7.76 <sup>f</sup>	
	6-pyrH	b	9.16 <sup>f</sup>	
	$\text{CH}_3$	3.40 <sup>g</sup>	3.45	$^3J_{\text{PtH}} = 20.3 \text{ Hz}$
	$\text{CH}_2$	3.75 <sup>g</sup>	3.66	
	5-pyrH	7.17 <sup>g</sup>	7.09	
	3-pyrH	7.33 <sup>g</sup>	7.35	$^3J_{\text{PtH}} = 36.8 \text{ Hz}$
	4-pyrH	7.70 <sup>g</sup>	7.75	
	6-pyrH	9.06 <sup>g</sup>	9.25	
	$\beta\text{-CH}_2$	b	2.60-2.79	$^3J_{\text{PtH}} = 28.8 \text{ Hz}$
	$\alpha\text{-CH}_2$	b	3.59-4.04	
	$\text{CH}$	b	3.59-4.04	
	$\text{CH}_3$	b	3.79	
	3-pyrH	b	7.21-7.39	
	5-pyrH	b	7.21-7.39	
	4-pyrH	b	7.69	
	6-pyrH	b	9.09	

Table II. Proton NMR spectral data for the Pt(II) complexes and comparison with the Pd(II) analogs (continued).

Compound	Assignment	Pd(II)	Pt(II)	$ ^nJ_{\text{PtH}} $
	$\alpha\text{-CH}_2$	b	2.12-2.30	
	$\text{CH}_3$	2.75, 3.26 <sup>h</sup>	2.83, 3.29	
	$\beta\text{-CH}_2$	b	2.93-3.74	
	3-pyrH	b	7.06-7.44	
	5-pyrH	b	7.06-7.44	
	4-pyrH	b	7.72	
	6-pyrH	b	8.91	$^3J_{\text{PtH}} = 40.4 \text{ Hz}$

a) Shifts are reported in ppm downfield from TMS and spectrum were taken in  $\text{CDCl}_3$ , unless otherwise noted. b) Data not reported. c)  $\text{Me}_2\text{SO-}d_6$ . d) Ref. 119. e) Ref. 98. f) In  $\text{Me}_2\text{SO-}d_6$   $\delta$  3.74 ( $\text{CH}_3$ ), 4.20 ( $\text{CH}_2$ ), 5.12 ( $\text{CH}$ ), 7.44-7.58 (3,5-pyrH), 7.93 (4-pyrH), 8.88 (6-pyrH),  $^3J_{\text{PtH}} = 32.2 \text{ Hz}$ . g) Ref. 103. h) Ref. 104.

### Proton NMR Spectroscopy of the Pt(IV) Complexes

Probably the most significant aspect of the  $^1\text{H}$  NMR spectra of the Pt(IV) complexes is the fact that  $^{195}\text{Pt}-\text{H}$  coupling constants are generally about 30% less than corresponding Pt(II) complexes<sup>113</sup> due to decreased electron density on the Pt(IV) atom. In these Pt(IV) complexes the average  $^nJ_{\text{PtH}}$ -values are:  $^2J = 89.5$  Hz,  $^3J = 14.2$  Hz, with an average decrease of 67% supporting the proposed Pt(IV) structures.

Another interesting trend is that the PtCH proton shifts downfield by an average of 0.26 ppm for the symmetrical Pt(IV) complexes. Also H-2(6) shifts downfield relative to the Pt(II) complexes with an average downfield shift of 0.44 ppm and a range of 10.53-10.89 ppm. These shifts are due to the increased electron-withdrawing ability of Pt(IV) over Pt(II).

The  $^2J_{\text{PtH}}$  coupling constants for the Pt(IV) complexes range from 84.7 to 98.9 Hz confirming the fact that C-bonding is maintained during oxidation. The average decrease in  $^2J_{\text{PtH}}$  as compared with the Pt(II) complexes is 30% as expected for Pt(IV) complexes.<sup>113</sup>

The structure of the unsymmetrical *cis*(dichloro)-*cis*(dimethyl malonato-C)-1,10-phenanthrolineplatinum(IV) (73) was assigned based on its  $^1\text{H}$  NMR spectrum which has four different methoxy peaks ranging from  $\delta$  2.56-3.84. The fact that four signals rather than two averaged signals were observed indicates hindered rotation (on the NMR time scale) about the Pt-C bond in this complex, probably due to a malonate-malonate steric interaction. In addition, the phenanthroline moiety showed two ortho proton signals ( $\delta$  10.60 and 10.87;  $^3J_{\text{PtH}} = 20.0$  and 30.5 Hz, respectively).

Complete  $^1\text{H}$  NMR spectral data for the Pt(IV) complexes are presented in Table III.

Table III. Proton NMR spectral data for the Pt(IV) complexes.<sup>a</sup>

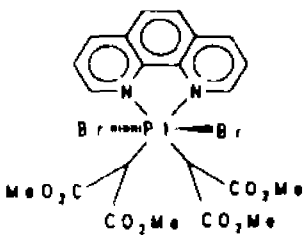
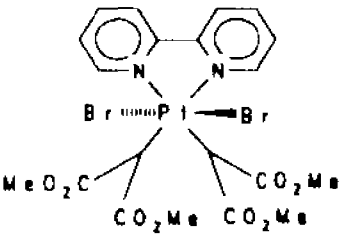
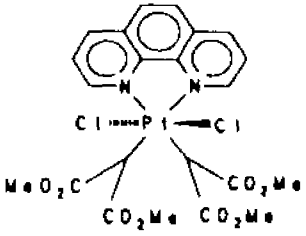
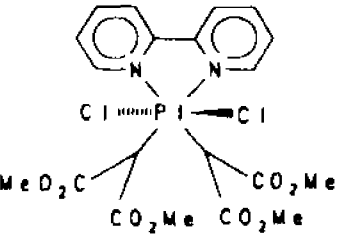
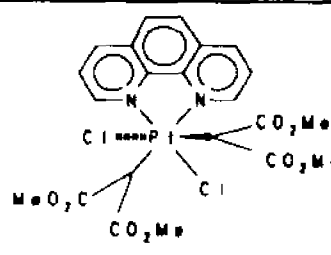
Compound	Assignment	Shift	$ ^nJ_{\text{PtH}} $
	$\text{CH}_3$	3.76	$^5J_{\text{PtH}} = 3.0 \text{ Hz}$
	$\text{CH}$	5.04	$^2J_{\text{PtH}} = 90.3 \text{ Hz}$
	5-phenH	7.96	
	3-phenH	8.00	
	4-phenH	8.49	
	2-phenH	10.89	$^3J_{\text{PtH}} = 15.4 \text{ Hz}$
	$\text{CH}_3$	3.72	
	$\text{CH}$	4.94	$^2J_{\text{PtH}} = 89.9 \text{ Hz}$
	5-pyrH	7.59-7.77	
	3,4-pyrH	8.02-8.29	
	6-pyrH	10.53	$^3J_{\text{PtH}} = 14.1 \text{ Hz}$
	$\text{CH}_3$	3.73	$^5J_{\text{PtH}} = 2.7 \text{ Hz}$
	$\text{CH}$	5.09	$^2J_{\text{PtH}} = 88.7 \text{ Hz}$
	5-phenH	7.95	
	3-phenH	8.01	
	4-phenH	8.50	
	2-phenH	10.88	$^3J_{\text{PtH}} = 14.6 \text{ Hz}$
	$\text{CH}_3$	3.72	
	$\text{CH}$	4.93	$^2J_{\text{PtH}} = 89.1 \text{ Hz}$
	5-pyrH	7.60-7.78	
	3,4-pyrH	7.91-8.18	
	6-pyrH	10.53	$^3J_{\text{PtH}} = 12.8 \text{ Hz}$

Table III. Proton NMR spectral data for the Pt(IV) complexes<sup>a</sup> (continued).

Compound	Assignment	Shift	$ ^nJ_{\text{PtH}} $
 (H2 cis to dmm)	$\text{CH}_3$	2.56 3.58 3.73 3.84	
	$\text{CH}$	4.52 5.87	$^2J_{\text{PtH}} = 84.7 \text{ Hz}$ $^2J_{\text{PtH}} = 98.9 \text{ Hz}$
	3,5,6,8-phenH	7.92-8.16	
	7-phenH	8.60	
	4-phenH	8.62	
	2-phenH	10.60	$^3J_{\text{PtH}} = 20.0 \text{ Hz}$
	9-phenH	10.87	$^3J_{\text{PtH}} = 30.5 \text{ Hz}$

a. All spectra were taken in  $\text{CDCl}_3$ .

### Carbon-13 NMR Spectroscopy of the Pt(II) Complexes

The first thing that is apparent in the  $^{13}\text{C}$  NMR spectra of the complexes is the enhanced  $^{195}\text{Pt}$  coupling over that seen in the  $^1\text{H}$  NMR spectra. The pyridine/dipyridine complexes show a  $^4J_{\text{PtC}}$  coupling to C-4 of the ring ranging from 6.5 to 9.7 Hz. Two different  $^3J$  coupling constants are possible: C-3 and C-5. Of the two, the phenanthroline complex only showed a coupling in C-3:  $^3J_{\text{PtC}} = 29.0$  Hz. On first inspection both of these coupling constants would be expected to be similar, however, in these pyridine/dipyridine complexes C-5 has a larger coupling constant than does C-3. For the five-membered chelated pyridine/dipyridine complexes,  $\Delta^3J$  ( $J_{\text{C5}} - J_{\text{C3}}$ ) range is 7.8-9.7 Hz, *very close to the*  $^4J$  range (6.5-9.7 Hz), suggesting that for C-5 there is only one pathway for coupling: Pt-N-C(6)-C(5). But for C-3 there are *two* pathways for coupling: Pt-N-C(2)-C(3) and Pt-N'-C(2')-C(2)-C(3) [Pt- $\beta\text{C}$ - $\alpha\text{C}$ -C(2)-C(3) for **69a**], a *four* bond route (see Figure 6). Assuming these four bond and three bond coupling constants are of opposite sign and are additive then the observed coupling constants for C-3 are the expected ones. Sarneski et al. have recently proposed<sup>120</sup> additive multi-path couplings such as this between platinum and carbon in small ring systems. Based upon the valid assumption that, for  $^nJ$ , when  $n$  is even the coupling constants are of one sign and when  $n$  is odd they are of the opposite sign, then, where two different paths are available for coupling, if the summation of  $n$  is even (both odd or both even) then the observed coupling constant will be the *sum* of the absolute values of the two constants and larger than expected. If the summation of  $n$  is odd (one odd and one even), then the observed coupling constant will be the *difference* of the absolute values of the two separate constants and substantially less than expected.

In complex **69b**,  $^3J$  for C-5 is *larger* than for C-3 and  $\Delta^3J$  is even greater (23.5

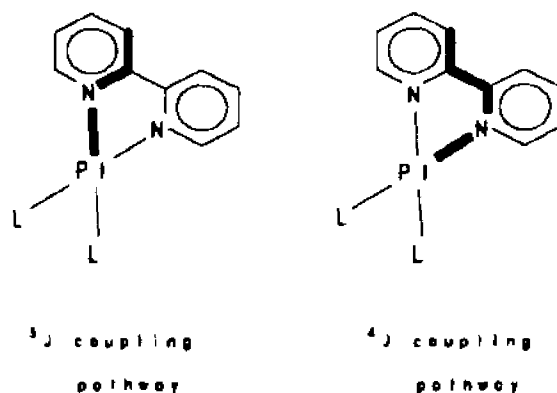


Figure 6. Three and Four Bond Coupling Routes to C-3 for the  $N,N'$ -Chelates.

Hz). In this case there exists a 3-bond and a 5-bond path for  $^{195}\text{Pt}$  coupling to C-3. Assuming the signs for these two constants are the same then the sum of the two paths gives the larger observed coupling constant. The two bond coupling constants to C-2(6) are similar in all of the Pt(II) complexes with a range of 30.5 to 34.0 Hz.

In complex **69a**, the  $\alpha$ -pyridyl carbon showed a two bond (or a two and a three bond) coupling to  $^{195}\text{Pt}$  of 17.4 Hz, substantially less than the two bond coupling constants to C-2 and C-6 (37.5 and 30.5 Hz, respectively); however, in **69b**, the corresponding three bond (or two three bond paths) coupling constant to the  $\alpha$ -pyridyl carbon was 132.0 Hz and the  $\beta$ -carbon has an aggregate four bond and two bond coupling constant of 43.5 Hz. The differences seen here are probably an effect of the six-membered ring conformation and Karplus effects. The four-bond path for the  $\beta$ -carbon is probably negligible because of the bond angles, whereas the two three-bond paths both have a dihedral angle of nearly zero (see X-ray discussion) thereby maximizing the Karplus effect. This result again supports the theory of multi-path additive coupling constants.<sup>120</sup>

Of course the largest coupling constants are the one-bond Pt-C coupling constants which can be grouped into two ranges: cyclometalated complexes (448.0-453.2 Hz) and the acyclic cis metalated complexes (634-635 Hz). The main effect here is the

differing trans effects, but also the non-cyclometalated complexes are more flexible and allow maximum Pt-C orbital overlap and, thus, the larger coupling constants.

In the *N,N'*-chelated complexes, the PtC resonances appeared at 19.7 and 18.8 ppm for **71a** and **71b**, respectively, relative to  $\approx 40$  ppm for Hdmm. For the *C,N*-chelated complexes the carbon bonded to the Pt resonated at  $\delta$  49.3 and 41.4 for **69a** and **69b**, respectively, compared with  $\delta$  49.9 and 50.8 for the ligands. This difference in  $\Delta\delta$ 's between the *N,N'*- and *C,N*-chelates is probably due to different trans effects.

Before a comparison of the MC shifts for Pd(phen)(dmm)<sub>2</sub> and Pd(dipy)(dmm)<sub>2</sub> can be made, the literature values<sup>98,100</sup> *must be reassigned* to 25.6 and 25.4 ppm, respectively. A comparison then shows a slight *upfield* shift (average 6.2 ppm) in the Pt complexes. This *upfield* shift was also seen in the *C,N*-chelated complexes with an average shift of 4.2 ppm. All other chemical shifts (Table IV) are as expected and very close to the Pd analogues (largest  $\Delta\delta$  = 2.2 ppm).



Table IV. Carbon-13 NMR spectral data for the Pt(II) complexes and comparison with the Pd(II) analogs.<sup>a</sup>

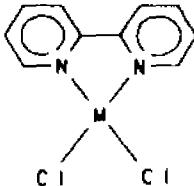
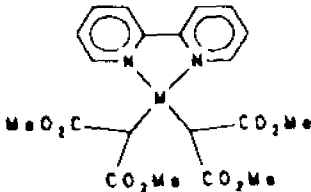
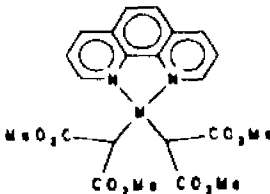
Compound	Assignment	Pd(II)	Pt(II)	$ ^nJ_{\text{PtC}} $
	C3		124.2 <sup>b</sup>	$^3J_{\text{PtC}} = 30.6 \text{ Hz}$
	C5		127.7 <sup>b</sup>	$^3J_{\text{PtC}} = 38.4 \text{ Hz}$
	C4		140.5 <sup>b</sup>	$^4J_{\text{PtC}} = 9.7 \text{ Hz}$
	C6		148.5 <sup>b</sup>	$^2J_{\text{PtC}} = 33.3 \text{ Hz}$
	C2		c	
	CH	25.0 <sup>d,e</sup>	19.7	$^1J_{\text{PtC}} = 635 \text{ Hz}$
	CH <sub>3</sub>	50.9 <sup>e</sup>	51.5	
	C3	121.6 <sup>e</sup>	122.5	$^3J_{\text{PtC}} = 18.2 \text{ Hz}$
	C5	126.4 <sup>e</sup>	127.6	$^3J_{\text{PtC}} = 27.9 \text{ Hz}$
	C4	138.9 <sup>e</sup>	138.9	$^4J_{\text{PtC}} = 6.5 \text{ Hz}$
	C6	153.1 <sup>e</sup>	153.8	$^2J_{\text{PtC}} = 32.2 \text{ Hz}$
	C2	155.4 <sup>e</sup>	157.0	
	CO	174.8 <sup>e</sup>	177.0	
	CH	25.3 <sup>d,e</sup>	18.8	$^1J_{\text{PtC}} = 634 \text{ Hz}$
	CH <sub>3</sub>	50.9 <sup>e</sup>	50.7	
	C3	125.2 <sup>e</sup>	125.4	$^3J_{\text{PtC}} = 29.0 \text{ Hz}$
	C5	126.9 <sup>e</sup>	126.9	
	C4a	129.3 <sup>e</sup>	129.6	
	C4	137.8 <sup>e</sup>	137.5	
	C10a	146.0 <sup>e</sup>	147.0	
	C2	153.2 <sup>e</sup>	152.9	$^2J_{\text{PtC}} = 34 \text{ Hz}$
	CO	174.9 <sup>e</sup>	176.2	$^2J_{\text{PtC}} = 64 \text{ Hz}$

Table IV. Carbon-13 NMR spectral data for the Pt(II) complexes and comparison with the Pd(II) analogs<sup>a</sup> (continued).

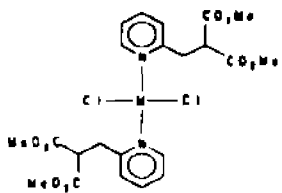
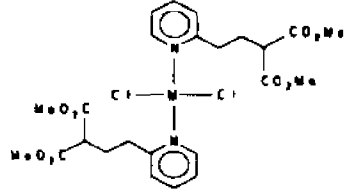
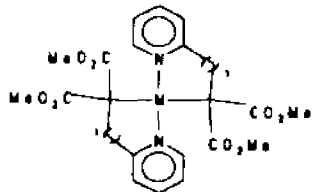
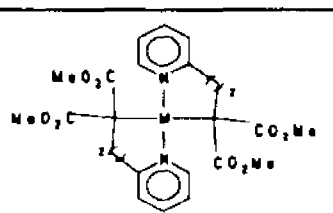
Compound	Assignment	Pd(II)	Pt(II)	$ ^aJ_{PtC} $
	CH <sub>2</sub>	f	37.0 <sup>b</sup>	
	CH	f	49.9 <sup>b</sup>	
	CH <sub>3</sub>	f	52.8 <sup>b</sup>	
	C5	f	124.3 <sup>b</sup>	
	C3	f	127.7 <sup>b</sup>	
	C4	f	139.3 <sup>b</sup>	
	C6	f	153.8 <sup>b</sup>	
	C2	f	159.6 <sup>b</sup>	
	CO	f	168.9 <sup>b</sup>	
	B-CH <sub>2</sub>	f	27.7 <sup>b</sup>	
	α-CH <sub>2</sub>	f	36.0 <sup>b</sup>	
	CH	f	50.5 <sup>b</sup>	
	CH <sub>3</sub>	f	52.3 <sup>b</sup>	
	C-5	f	123.3 <sup>b</sup>	
	C-3	f	126.0 <sup>b</sup>	
	C-4	f	139.1 <sup>b</sup>	
	C-6	f	153.7 <sup>b</sup>	
	C-2	f	163.0 <sup>b</sup>	
	CO	f	169.5 <sup>b</sup>	
	CH <sub>2</sub>	43.1 <sup>g</sup>	44.1	$^2J_{PtC} = 17.4 \text{ Hz}$
	PtC	53.6 <sup>g</sup>	49.3	$^1J_{PtC} = 453.2 \text{ Hz}$
	CH <sub>3</sub>	51.0 <sup>g</sup>	50.8	
	C3	120.6 <sup>g</sup>	120.7	$^3J_{PtC} = 33.8 \text{ Hz}$
	C5	121.2 <sup>g</sup>	121.5	$^3J_{PtC} = 42.0 \text{ Hz}$
	C4	138.0 <sup>g</sup>	137.4	$^4J_{PtC} = 8.7 \text{ Hz}$
	C6	151.7 <sup>g</sup>	151.8	$^2J_{PtC} = 30.5 \text{ Hz}$
	C2	171.8 <sup>g</sup>	172.7	$^2J_{PtC} = 37.5 \text{ Hz}$
	CO	173.7 <sup>g</sup>	174.6	$^2J_{PtC} = 47.9 \text{ Hz}$

Table IV. Carbon-13 NMR spectral data for the Pt(II) complexes and comparison with the Pd(II) analogs<sup>a</sup> (continued).

Compound	Assignment	Pd(II)	Pt(II)	$ ^nJ_{\text{PtC}} $
	$\alpha\text{-C}$	28.6 <sup>h</sup>	28.9	$^3J_{\text{PtC}} = 43.5 \text{ Hz}$
	PtC	45.6 <sup>h</sup>	41.4	$^1J_{\text{PtC}} = 448.0 \text{ Hz}$
	$\beta\text{-C}$	42.4 <sup>h</sup>	41.8	$^2J_{\text{PtC}} = 132.0 \text{ Hz}$
	$\text{CH}_3$	49.6 <sup>h</sup>	49.7	
		50.5 <sup>h</sup>	50.6	
	C5	121.5 <sup>h</sup>	122.0	$^3J_{\text{PtC}} = 49.9 \text{ Hz}$
	C3	122.3 <sup>h</sup>	122.5	$^3J_{\text{PtC}} = 26.4 \text{ Hz}$
	C4	137.6 <sup>h</sup>	137.2	$^4J_{\text{PtC}} = 9.2 \text{ Hz}$
	C6	151.3 <sup>h</sup>	152.3	
	C2	162.8 <sup>h</sup>	163.3	$^2J_{\text{PtC}} = 10.4 \text{ Hz}$
	CO	173.7 <sup>h</sup>	174.5	$^2J_{\text{PtC}} = 56.3 \text{ Hz}$
		175.9 <sup>h</sup>	176.5	$^2J_{\text{PtC}} = 63.9 \text{ Hz}$

a) All spectra were taken in  $\text{CDCl}_3$ , unless otherwise noted. b) In  $\text{Me}_2\text{SO}-d_6$ . c) Not observed. d) Incorrectly reported in the literature. e) Reference 98. f) Not reported in the literature. g) Reference 103. h) Reference 104.

### Carbon-13 of the Pt(IV) Complexes

Only one, two, and three bond  $^{195}\text{Pt}$  coupling constants were observed in the Pt(IV) complexes. In the phenanthroline complexes, the  $^3J$   $^{195}\text{Pt}$ -(3-phenC) coupling constants were *larger* (18.6, 18.3 Hz) than for  $^2J$  (15.0, 14.0 Hz); no other ring coupling was observed. In the dipyridine complexes, the  $^{195}\text{Pt}$ -(3-pyrC) coupling constants were again smaller than those for C-5. This is also due to the fact that two different paths for coupling were available to C-3.

In the dibromo complexes the malonate moiety showed carbonyl carbon coupling to  $^{195}\text{Pt}$  of 44.3 and 43.0 Hz for  $\text{Pt}(\text{phen})(\text{dmm})_2\text{Br}_2$  and  $\text{Pt}(\text{dipy})(\text{dmm})_2\text{Br}_2$ , respectively. The largest coupling constants were for  $^{195}\text{Pt}$ -C ranging from 556.5 to 560.5 Hz. The average (558.5 Hz) was 88% that of the Pt(II) complexes (634 Hz) substantiating the proposed structure of the oxidation products.

Complete  $^{13}\text{C}$  NMR spectral data for the Pt(IV) complexes are presented in Table V.

Table V. Carbon-13 NMR spectral data for the Pt(IV) complexes.<sup>a</sup>

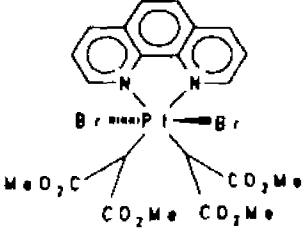
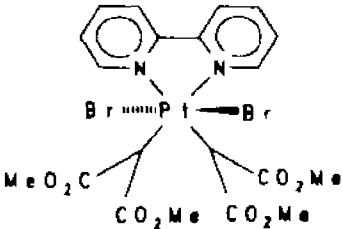
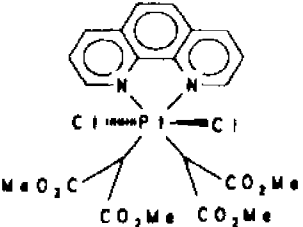
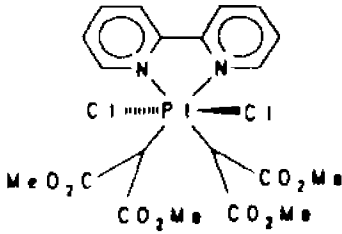
Compound	Assignment	Shift	$ ^nJ_{\text{PtC}} $
	CH	21.1	$^1J_{\text{PtC}} = 560 \text{ Hz}$
	CH <sub>3</sub>	50.8	
	C3	126.4	$^3J_{\text{PtC}} = 18.6 \text{ Hz}$
	C5	127.5	
	C4a	131.0	
	C4	139.0	
	C10a	146.0	
	C2	156.0	$^2J_{\text{PtC}} = 15.0 \text{ Hz}$
	CO	174.5	$^2J_{\text{PtC}} = 44.3 \text{ Hz}$
	CH	21.0	$^1J_{\text{PtC}} = 556.7 \text{ Hz}$
	CH <sub>3</sub>	50.8	
	C3	123.1	$^3J_{\text{PtC}} = 12.1 \text{ Hz}$
	C5	127.1	$^3J_{\text{PtC}} = 18.1 \text{ Hz}$
	C4	140.2	
	C6	155.9	$^2J_{\text{PtC}} = 14.5 \text{ Hz}$
	C2	157.7	$^2J_{\text{PtC}} = 16.1 \text{ Hz}$
	CO	174.3	$^2J_{\text{PtC}} = 43.0 \text{ Hz}$
	CH	23.9	$^1J_{\text{PtC}} = 560.6 \text{ Hz}$
	CH <sub>3</sub>	50.9	
	C3	125.9	$^3J_{\text{PtC}} = 18.3 \text{ Hz}$
	C5	127.5	
	C4a	131.0	
	C4	139.1	
	C2	155.5	$^2J_{\text{PtC}} = 14.0 \text{ Hz}$
	CO	173.8	
	C10a	b	

Table V. Carbon-13 NMR spectral data for the Pt(IV) complexes<sup>a</sup> (continued).

Compound	Assignment	Shift	$ ^nJ_{\text{PtC}} $
	CH	21.0	$^1J_{\text{PtC}} = 556.5 \text{ Hz}$
	CH <sub>3</sub>	50.9	
	C3	123.0	$^3J_{\text{PtC}} = 12.2 \text{ Hz}$
	C5	127.1	$^3J_{\text{PtC}} = 18.0 \text{ Hz}$
	C4	140.2	
	C2	155.2	
	C6	156.0	$^2J_{\text{PtC}} = 14.3 \text{ Hz}$
	CO	174.4	

a) All spectra were run in CDCl<sub>3</sub>. b) Not observed.

### Infrared Spectra of the Platinum Complexes

The C=O stretching frequency in the IR spectrum of a malonato complex is an excellent indicator of the mode of bonding. For C-bonded complexes, this absorption ranges from 1670-1730  $\text{cm}^{-1}$  and for O,O'-chelation, the range is generally below 1600  $\text{cm}^{-1}$ . Thus, as expected, the delocalization which occurs in O,O'-chelation shifts the carbonyl stretching frequency to longer wavelengths whereas C-bonding has a negligible effect. For these platinum complexes, the C=O stretching absorptions occurred in the range of 1686-1750  $\text{cm}^{-1}$  corresponding to the general range for C-bonded complexes.

Table VI. Diagnostic Pt IR absorptions.

Compound	C=O	C-O	Ligand
Pt(five) <sub>2</sub>	1686	1181	
Pt(six) <sub>2</sub>	1690	1196	
Pt(dipy)(dmm) <sub>2</sub>	1744	1136	783, 729
Pt(phen)(dmm) <sub>2</sub>	1725	1138	841, 716
Pt(dipy)(dmm) <sub>2</sub> Br <sub>2</sub>	1744	1127	778, 732
Pt(phen)(dmm) <sub>2</sub> Br <sub>2</sub>	1746	1144	845, 716
Pt(dipy)(dmm) <sub>2</sub> Cl <sub>2</sub>	1740	1127	762, 727
Pt(phen)(dmm) <sub>2</sub> Cl <sub>2</sub>	1744	1129	847, 718

### Structural Characterization of the Cyclometalated Pt(II) Complexes

To determine the salient structural features in the cyclometalated complexes (**69a** and **69b**) such as Pt-C and Pt-N bond distances and chelate bond angles, single crystal X-ray structure determinations were undertaken and the crystal data are given in Table VII. Important bond distances and angles for **69a** are presented in Tables VIII and IX, respectively, and an ORTEP drawing is shown in Figure 7.

For the trans complex **69a**, the Pt-coordination is square planar with a slight distortion. The ligating atoms are tetrahedrally arranged each lying 0.1 Å out-of-the-best-plane defined by the four atoms [N(1), N(2), C(7), C(18)]. The Pt atom lies on the line defined by the nitrogen atoms [N(1)-Pt-N(2): 178.4(4)°] with the carbon atoms tetrahedrally displaced [C(7)-Pt-C(18): 169.6(2)°].

The Pt-N bond distances are 2.013(5) and 2.021(5) Å as compared to 2.040(3) and 2.042(3) Å in the Pd(II) analogue.<sup>103</sup> The Pt-C bond distances are 2.142(6) and 2.159(6) Å, identical to the corresponding distances in the Pd(II) analogue.<sup>103</sup> The chelation angles about Pt [N(1)-Pt-C(7) and N(2)-Pt-C(18)] are 10° less than the 90° square planar arrangement [80.6(2)° and 80.4(2)°, respectively]. Newkome et al. have reported a correlation between the M-C-CH<sub>2</sub> chelate angle and the <sup>13</sup>C NMR chemical shift of the central carbon for the Pd(II) complexes.<sup>100</sup> The Pt(II) complexes reported here also fit this correlation.

The bond distances and angles in the pyridine rings are all normal. The pyridine rings are planar and form a dihedral angle of 60° with each other and each being ≈30° rotated from the coordination plane in opposite directions. The conformations of both of the five-membered chelate rings are envelopes [Pt-N(1)-C(5)-C(6) = -2.6°; Pt-N(2)-C(16)-C(17) = -0.2°] with the metalated carbons [C(7) and C(18)] forming the flaps, both of which lie on the same face of the coordination plane.

Important bond distances and angles for **69b** are presented in Tables VIII and IX.



respectively, and an ORTEP drawing is shown in Figure 8. The Pt coordination is square planar with a slight, but definite, tetrahedral distortion. The platinum atom lies on-the-best-plane defined by the ligating atoms [N(1), N(2), C(8), C(20)] plus platinum with the carbon atoms lying 0.18 Å above-the-best-plane and the nitrogen atoms lying 0.16 Å below it giving the tetrahedral distortion. The N(1)-Pt-N(2) and C(8)-Pt-C(20) angles are 172.2(1) and 169.2(1)°, respectively.

The Pt-N bond distances are 2.013(3) and 2.021(3) Å as compared to 2.038(7) and 2.037(7) Å in the corresponding Pd(II) analogue.<sup>104</sup> The Pt-C bond distances are 2.176(3) and 2.159(3) Å in close agreement with those in the Pd(II) analogue<sup>104</sup> [2.190(9) and 2.172(9) Å]. The chelation angles about Pt [N(1)-Pt-C(8) and N(2)-Pt-C(20)] are again less than the expected 90° for a square planar arrangement [84.9(1) and 83.7(1)°, respectively]. The pyridine rings are planar and form a torsion angle of 56.8° with each other; each of the pyridine rings is rotated ca. 61° from the coordination plane.

The six-membered chelate rings are in "pseudo" boat conformations [Pt-N(1)-C(5)-C(6) = 0.14°; Pt-C(8)-C(7)-C(6) = 12.57°; Pt-N(2)-C(17)-C(18) = 2.93°; Pt-C(20)-C(19)-C(18) = 23.01°] with Pt and C(6) as apexes in one chelate and Pt and C(18) as apexes in the other.

The two methoxy groups of each ligand are clearly in different environments with one being over the opposite pyridine ring thus structurally supporting the large *upfield* shift observed in the <sup>1</sup>H NMR spectrum ( $\delta$  = 2.83).

Because of the unusual structure of **70**, an X-ray crystal structure was needed to clarify the structure. Crystal data for **70** are presented in Table VII and important bond lengths and angles are given in Tables X and XI, respectively; an ORTEP drawing is shown in Figure 9.

Complex **70** is a diacetate bridged dimer with a Pt-Pt distance of 3.1170(5) Å

which is slightly longer ( $\approx 0.1$  Å) than related structures<sup>121</sup> and far longer than complexes containing a Pt-Pt bond (2.495-2.557 Å).<sup>122</sup> The Pt-atoms have square planar coordination and the Pt-N bond distances [2.034(7), 1.996(7) Å] are very close to those in complex **69a** [2.013(5), 2.021(5) Å] but the Pt-C distances [2.069(9), 2.061(9) Å] are slightly shorter than in **69a** [2.159(6), 2.142(6) Å]. The two pyridyl ligands are arranged in an anti sense in the dimer accounting for the upfield shift of one of the  $\text{OCH}_3$  moieties in the  $^1\text{H}$  NMR spectrum because of shielding caused by the opposite pyridine ring.<sup>123</sup> The five-membered chelate rings are in envelope conformations with the metallated carbons being the flaps as shown by the torsion angles Pt(1)-N(1)-C(9)-C(10) ( $0.0^\circ$ ) and Pt(2)-N(2)-C(20)-C(21) ( $-1.1^\circ$ ). The chelate angles are similar to those in **69a**.

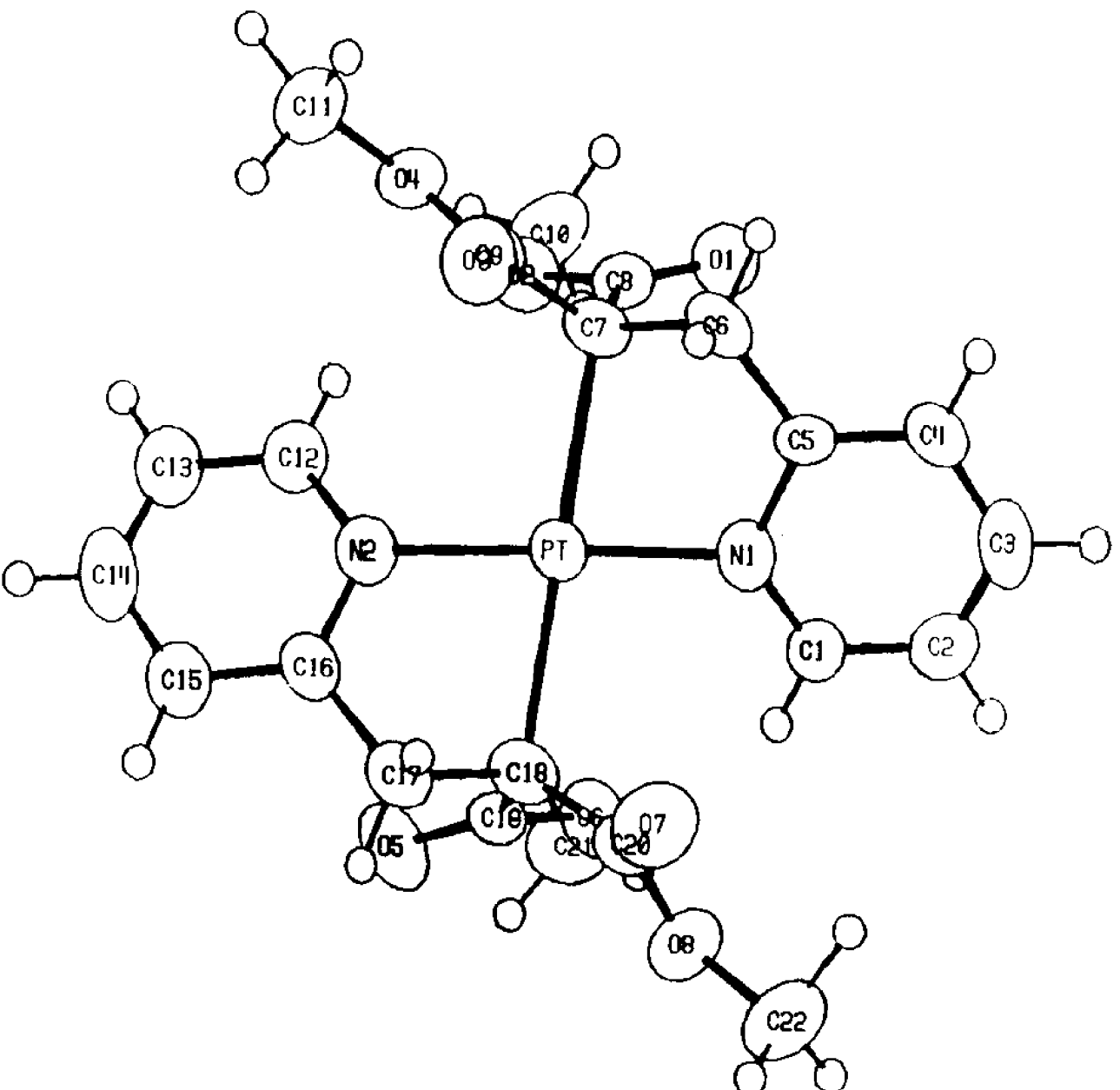


Figure 7. ORTEP Drawing of  $C_{22}H_{24}N_2O_8Pt$ .

Table VII. Crystal data and data collection parameters for  $C_{22}H_{24}N_2O_8Pt$ ,  $C_{24}H_{28}N_2O_8Pt$  and  $C_{26}H_{30}N_2O_{12}Pt_2$ .

Compound:	<b>69a</b>	<b>69b</b>	<b>70</b>
Formula:	$C_{22}H_{24}N_2O_8Pt$	$C_{24}H_{28}N_2O_8Pt$	$C_{26}H_{30}N_2O_{12}Pt_2$
Formula Wt:	639.5	667.6	952.7
Crystal System:	monoclinic	monoclinic	monoclinic
Space Group:	$P2_1/c$	$P2_1/n$	$P2_1/n$
$a$ , Å:	9.590(2)	10.0905(12)	10.446(5)
$b$ , Å:	29.594(7)	23.555(2)	16.669(3)
$c$ , Å:	8.442(2)	10.823(3)	17.038(3)
$\beta$ , deg.:	106.02(2)	106.23(2)	97.19(3)
$V$ , Å <sup>3</sup> :	2303(2)	2470(1)	2943(3)
$d$ , gcm <sup>-3</sup> :	1.845	1.795	2.150
$Z$ :	4	4	4
$T$ , °C:	20	25	25
$\mu$ (MoK $\alpha$ ), cm <sup>-1</sup> :	62.0	57.9	96.6
Crystal size, mm:	0.03x0.32x0.44	0.20x0.36x0.48	0.10x0.12x0.36
Color:	colorless	colorless	pale yellow
Min. rel. trans., %:	41.46	57.93	83.98
$2\theta$ limits, deg.:	$2 < 2\theta < 50$	$2 < 2\theta < 60$	$2 < 2\theta < 50$
Scan rates, deg. min <sup>-1</sup> :	0.39 - 4.0	0.91 - 4.0	0.53 - 4.0
Precision:	$I = 50\sigma(I)$	$I = 50\sigma(I)$	$I = 50\sigma(I)$
Max. scan time, s:	120	120	120
Unique Data:	4032	7186	5175
Observed Data:	2872	5237	3375
Criterion:	$I > 2\sigma(I)$	$I > 3\sigma(I)$	$I > 3\sigma(I)$
Variables:	298	317	379
$R$ :	0.036	0.026	0.032
$R_w$ :	0.037	0.029	0.030
Extinction:	—	$1.28(3) \times 10^{-7}$	—
Max. residual, eÅ <sup>-3</sup> :	0.98	0.91	1.16
Comments:		Isomorphous with Pd analog	

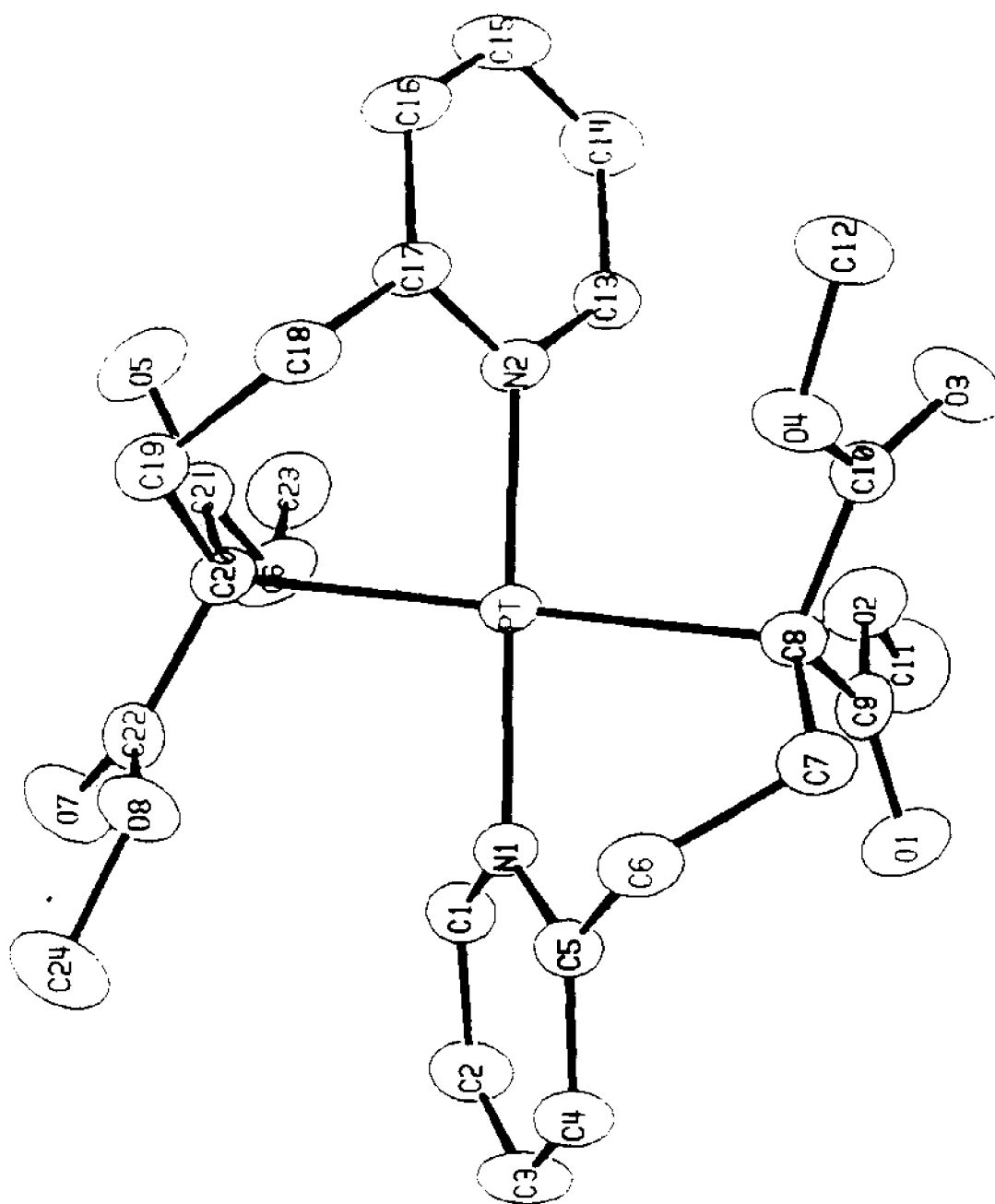


Figure 8. ORTEP Drawing of  $C_{24}H_{28}N_2O_8Pt$ .

Table VIII. Important bond distances (Å) for  $C_{22}H_{24}N_2O_8Pt$  and  $C_{24}H_{28}N_2O_8Pt$ .

Complex <b>69a</b>		Complex <b>69b</b>	
Pt-N(1)	2.013(5)	Pt-N(1)	2.013(3)
Pt-N(2)	2.021(5)	Pt-N(2)	2.021(3)
Pt-C(7)	2.159(6)	Pt-C(8)	2.176(3)
Pt-C(18)	2.142(6)	Pt-C(20)	2.159(3)

Table IX. Important bond angles (°) for  $C_{22}H_{24}N_2O_8Pt$  and  $C_{24}H_{28}N_2O_8Pt$ .

Complex <b>69a</b>			
N(1)-Pt-N(2)	178.4(2)	Pt-N(2)-C(12)	126.9(5)
Pt-N(2)-C(16)	114.8(4)	Pt-C(18)-C(17)	101.3(4)
Pt-C(18)-C(19)	106.1(4)	Pt-C(18)-C(20)	112.0(4)
Pt-C(7)-C(6)	101.6(4)	Pt-C(7)-C(8)	106.5(4)
Pt-C(7)-C(9)	110.2(4)	N(1)-Pt-C(7)	80.6(2)
N(1)-Pt-C(18)	98.3(2)	N(2)-Pt-C(7)	100.9(2)
N(2)-Pt-C(18)	80.4(2)	C(7)-Pt-C(18)	169.6(2)
Pt-N(1)-C(1)	127.0(5)	Pt-N(1)-C(5)	115.1(4)

Complex <b>69b</b>			
N(1)-Pt-N(2)	172.2(1)	Pt-C(8)-C(10)	105.5(2)
N(1)-Pt-C(8)	84.9(1)	N(1)-Pt-C(20)	96.1(1)
N(2)-Pt-C(8)	96.8(1)	N(2)-Pt-C(20)	83.7(1)
C(8)-Pt-C(20)	169.2(1)	Pt-N(1)-C(1)	119.5(2)
Pt-N(1)-C(5)	120.6(2)	Pt-N(2)-C(13)	119.7(2)
Pt-N(2)-C(17)	121.1(2)	Pt-C(20)-C(19)	108.9(2)
Pt-C(20)-C(21)	104.7(2)	Pt-C(20)-C(22)	108.8(2)
Pt-C(8)-C(7)	110.0(2)	Pt-C(8)-C(9)	102.3(2)

Table X. Important bond distances (Å) for  $C_{26}H_{30}N_2O_{12}Pt_2$ .

Pt(1)-Pt(2)	3.1179(5)	Pt(2)-O(1)	2.013(8)
Pt(1)-O(2)	2.106(6)	Pt(2)-O(3)	2.112(6)
Pt(1)-O(4)	2.009(7)	Pt(2)-N(2)	1.996(7)
Pt(1)-N(1)	2.034(7)	Pt(2)-C(22)	2.061(9)
Pt(1)-C(11)	2.069(9)		

Table XI. Important bond angles (°) for  $C_{26}H_{30}N_2O_{12}Pt_2$ .

Pt(2)-Pt(1)-O(2)	77.9(2)	Pt(1)-C(11)-C(10)	105.1(6)
Pt(2)-Pt(1)-O(4)	81.3(2)	Pt(1)-N(1)-C(9)	115.5(6)
Pt(2)-Pt(1)-N(1)	101.5(2)	Pt(1)-Pt(2)-N(2)	104.8(2)
Pt(2)-Pt(1)-C(11)	110.0(3)	Pt(1)-Pt(2)-C(22)	110.9(2)
O(2)-Pt(1)-O(4)	89.1(3)	O(1)-Pt(2)-O(3)	90.5(3)
O(2)-Pt(1)-N(1)	94.2(3)	O(1)-Pt(2)-N(2)	176.1(3)
O(2)-Pt(1)-C(11)	171.0(3)	O(1)-Pt(2)-C(22)	95.1(3)
O(4)-Pt(1)-N(1)	176.0(3)	O(3)-Pt(2)-N(2)	91.9(3)
O(4)-Pt(1)-C(11)	96.2(3)	O(3)-Pt(2)-C(22)	171.8(3)
N(1)-Pt(1)-C(11)	80.2(3)	N(2)-Pt(2)-C(22)	82.2(3)
Pt(1)-Pt(2)-O(1)	78.7(2)	Pt(2)-C(22)-C(21)	105.4(6)
Pt(1)-Pt(2)-O(3)	76.1(2)	Pt(2)-N(2)-C(20)	115.9(6)

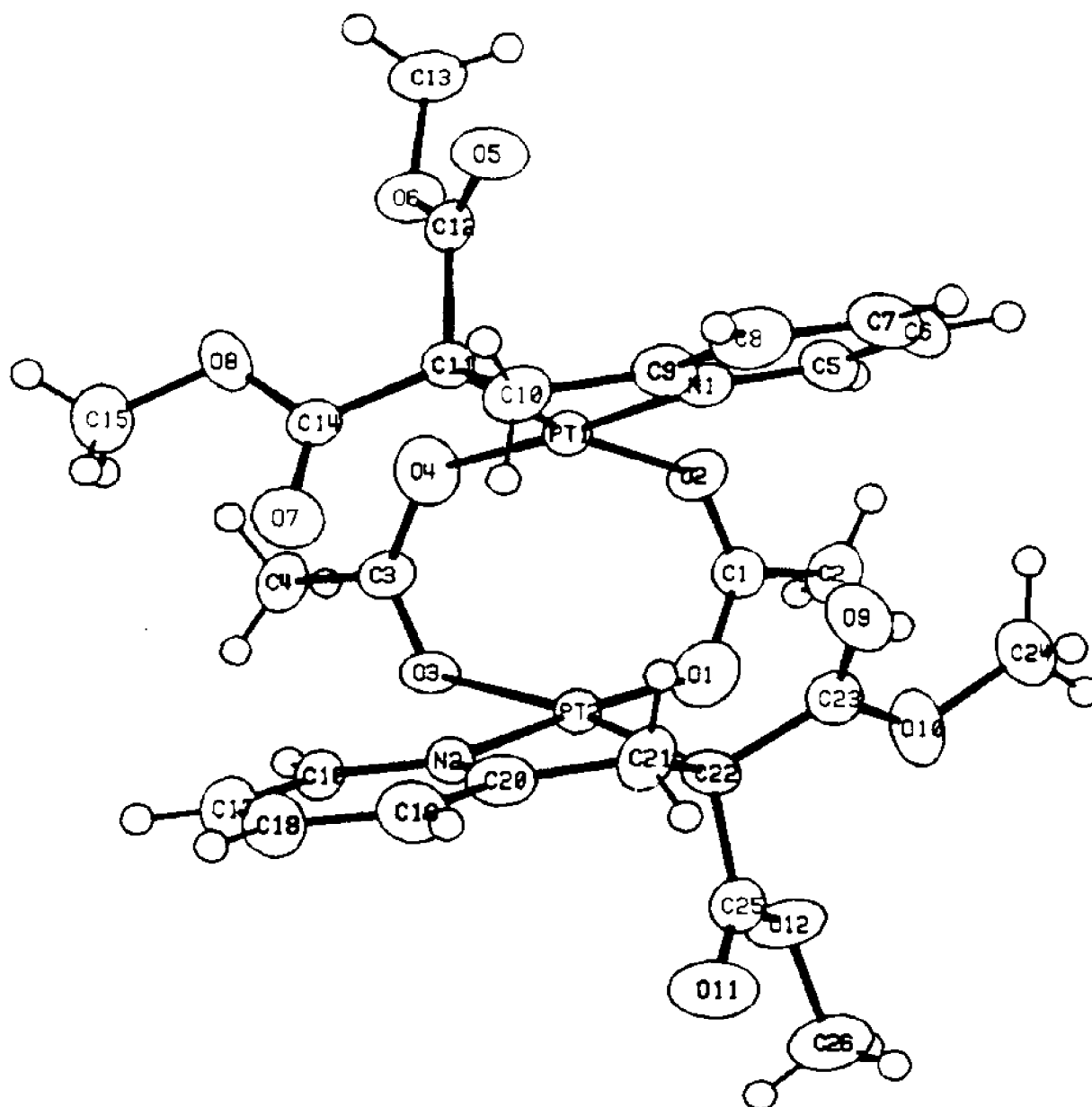


Figure 9. ORTEP Drawing of  $C_{26}H_{30}N_2O_{12}Pt_2$ .



Table XII. Coordinates for  $\text{Pt}(\text{C}_{11}\text{H}_{12}\text{NO}_4)_2$ .

Atom	x	y	z
Pt	0.41814(3)	0.12295(1)	0.25561(3)
O(1)	0.0834(7)	0.1716(2)	-0.0252(6)
O(2)	0.1341(6)	0.1001(2)	-0.0726(6)
O(3)	0.1470(7)	0.0771(2)	0.4210(6)
O(4)	0.0670(6)	0.0521(2)	0.1628(6)
O(5)	0.7578(7)	0.0830(2)	0.1666(7)
O(6)	0.6926(6)	0.1540(2)	0.1089(6)
O(7)	0.6754(7)	0.1655(2)	0.5924(6)
O(8)	0.7992(7)	0.1871(2)	0.4211(7)
N(1)	0.3887(7)	0.1902(2)	0.2607(7)
N(2)	0.4530(7)	0.0557(2)	0.2492(7)
C(1)	0.4731(9)	0.2219(3)	0.2280(10)
C(2)	0.4455(10)	0.2666(3)	0.2358(11)
C(3)	0.3283(11)	0.2804(3)	0.2840(11)
C(4)	0.2333(9)	0.2484(3)	0.3081(9)
C(5)	0.2619(8)	0.2035(2)	0.2934(8)
C(6)	0.1641(9)	0.1655(3)	0.3123(9)
C(7)	0.1850(8)	0.1247(3)	0.2064(8)
C(8)	0.1265(8)	0.1344(3)	0.0294(9)
C(9)	0.1328(9)	0.0834(3)	0.2747(9)
C(10)	0.0808(12)	0.1078(3)	-0.2434(10)
C(11)	0.0156(12)	0.0123(3)	0.2213(12)
C(12)	0.3713(10)	0.0258(3)	0.1473(9)
C(13)	0.4046(11)	-0.0182(3)	0.1461(11)
C(14)	0.5263(12)	-0.0340(3)	0.2533(12)
C(15)	0.6189(11)	-0.0038(3)	0.3555(11)
C(16)	0.5818(9)	0.0412(2)	0.3507(9)
C(17)	0.6729(9)	0.0774(3)	0.4467(10)
C(18)	0.6496(8)	0.1219(3)	0.3504(8)
C(19)	0.7076(8)	0.1175(2)	0.2048(9)
C(20)	0.7043(9)	0.1600(3)	0.4656(9)
C(21)	0.7319(11)	0.1498(3)	-0.0428(10)
C(22)	0.8545(13)	0.2237(3)	0.5343(13)

Table XIII. Coordinates for  $\text{Pt}(\text{C}_{12}\text{H}_{14}\text{NO}_4)_2$ .

Atom	x	y	z
Pt	0.18987(1)	0.12188(1)	0.18534(1)
O(1)	-0.0434(3)	0.2410(1)	0.1995(3)
O(2)	0.1063(3)	0.2497(1)	0.0829(3)
O(3)	-0.0061(4)	0.1846(1)	-0.1370(3)
O(4)	-0.0423(3)	0.0950(1)	-0.0895(3)
O(5)	0.5670(3)	0.0851(1)	0.2148(3)
O(6)	0.4965(3)	0.1538(1)	0.3225(3)
O(7)	0.4376(3)	0.0794(1)	0.5129(3)
O(8)	0.2535(3)	0.0261(1)	0.4227(3)
N(1)	0.1301(3)	0.1399(1)	0.3435(3)
N(2)	0.2669(3)	0.1131(1)	0.0330(3)
C(1)	0.2103(4)	0.1734(2)	0.4357(4)
C(2)	0.1695(5)	0.1915(2)	0.5398(4)
C(3)	0.0446(5)	0.1743(2)	0.5542(4)
C(4)	-0.0381(4)	0.1398(2)	0.4599(4)
C(5)	0.0040(4)	0.1239(2)	0.3519(4)
C(6)	-0.0836(4)	0.0932(2)	0.2402(4)
C(7)	-0.1255(4)	0.1315(2)	0.1202(4)
C(8)	-0.0057(4)	0.1601(2)	0.0809(3)
C(9)	0.0126(4)	0.2204(2)	0.1253(4)
C(10)	-0.0178(4)	0.1504(2)	-0.0582(4)
C(11)	0.1427(6)	0.3047(2)	0.1379(6)
C(12)	-0.0454(5)	0.0800(2)	-0.2186(4)
C(13)	0.3031(4)	0.1601(2)	-0.0235(4)
C(14)	0.3682(5)	0.1569(2)	-0.1188(4)
C(15)	0.3965(5)	0.1039(2)	-0.1605(4)
C(16)	0.3596(5)	0.0563(2)	-0.1036(4)
C(17)	0.2977(4)	0.0616(2)	-0.0049(4)
C(18)	0.2652(4)	0.0126(2)	0.0673(4)
C(19)	0.3516(4)	0.0120(2)	0.2094(4)
C(20)	0.3628(4)	0.0690(2)	0.2815(4)
C(21)	0.4871(4)	0.1013(2)	0.2714(4)
C(22)	0.3602(4)	0.0599(2)	0.4167(4)
C(23)	0.5967(5)	0.1916(2)	0.2941(5)
C(24)	0.2382(6)	0.0152(2)	

Table XIV. Coordinates for  $\text{Pt}_2\text{C}_{26}\text{H}_{30}\text{N}_2\text{O}_{12}$ .

Atom	x	y	z	Atom	x	y	z
PT(1)	0.04712(3)	0.10894(2)	0.11225(2)	C(6)	0.0108(10)	0.0984(7)	0.3603(6)
PT(2)	-0.12984(3)	0.25434(2)	0.05785(2)	C(7)	0.1070(10)	0.1480(7)	0.3919(6)
O(1)	-0.2616(7)	0.1685(5)	0.0698(4)	C(8)	0.1871(10)	0.1819(7)	0.3425(6)
O(2)	-0.1383(5)	0.0577(4)	0.1049(4)	C(9)	0.1632(8)	0.1669(6)	0.2628(5)
O(3)	-0.0887(6)	0.2021(4)	-0.0491(3)	C(10)	0.2437(9)	0.2015(6)	0.2022(6)
O(4)	0.0417(6)	0.0956(5)	-0.0053(4)	C(11)	0.2376(8)	0.1456(6)	0.1327(5)
O(5)	0.3744(6)	0.0594(5)	0.2192(4)	C(12)	0.3120(8)	0.0664(6)	0.1554(5)
O(6)	0.2952(6)	0.0092(4)	0.1011(4)	C(13)	0.3485(10)	-0.0661(6)	0.1258(7)
O(7)	0.2599(8)	0.2583(5)	0.0501(5)	C(14)	0.2777(8)	0.1882(6)	0.0621(5)
O(8)	0.3382(7)	0.1431(5)	0.0141(4)	C(15)	0.3717(12)	0.1834(9)	-0.0543(7)
O(9)	-0.1200(7)	0.2538(5)	0.2776(4)	C(16)	0.0481(9)	0.3604(6)	-0.0189(5)
O(10)	-0.3187(6)	0.2399(5)	0.2173(4)	C(17)	0.1335(10)	0.4226(7)	-0.0243(6)
O(11)	-0.2758(7)	0.4479(5)	0.1269(5)	C(18)	0.1630(10)	0.4694(7)	0.0407(7)
O(12)	-0.3914(6)	0.3384(4)	0.0996(4)	C(19)	0.1064(10)	0.4575(7)	0.1105(6)
N(1)	0.0661(6)	0.1213(5)	0.2319(4)	C(20)	0.0169(9)	0.3937(6)	0.1115(6)
N(2)	-0.0084(6)	0.3450(5)	0.0471(4)	C(21)	-0.0498(9)	0.3690(6)	0.1795(5)
C(1)	-0.2444(8)	0.0922(6)	0.0894(5)	C(22)	-0.1708(9)	0.3207(5)	0.1537(5)
C(2)	-0.3611(9)	0.0418(7)	0.0948(6)	C(23)	-0.1975(9)	0.2688(6)	0.2227(5)
C(3)	-0.0211(8)	0.1404(6)	-0.0620(5)	C(24)	-0.3431(11)	0.1845(8)	0.2769(7)
C(4)	-0.0117(9)	0.1207(7)	-0.1473(5)	C(25)	-0.2817(9)	0.3767(6)	0.1273(5)
C(5)	-0.0094(9)	0.0864(6)	0.2793(6)	C(26)	-0.5042(10)	0.3875(7)	0.0852(7)

## Conclusions

Several potential anti-tumor cis organoplatinum(II) complexes have been prepared which incorporate dimethyl malonato-C ligands. The Pt-C bonding was substantiated by  $^1\text{H}$  and  $^{13}\text{C}$  NMR chemical shift and coupling data as well as by IR (C=O) data. These complexes were readily oxidized with either  $\text{Br}_2$ ,  $\text{Cl}_2$ ,  $\text{CuBr}_2$ , or  $\text{CuCl}_2$  to give the corresponding organoplatinum(IV) complexes. In addition, two new trans *C,N*-cyclometalated platinum(II) complexes were made from 2-pyridyl ligands having dimethyl malonate pendants for metalation. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of all complexes were studied and compared to their corresponding Pd(II) complexes.<sup>100</sup> X-ray crystal structures of the cyclometalated complexes proved the presence of trans Pt-C bonding.

## Experimental

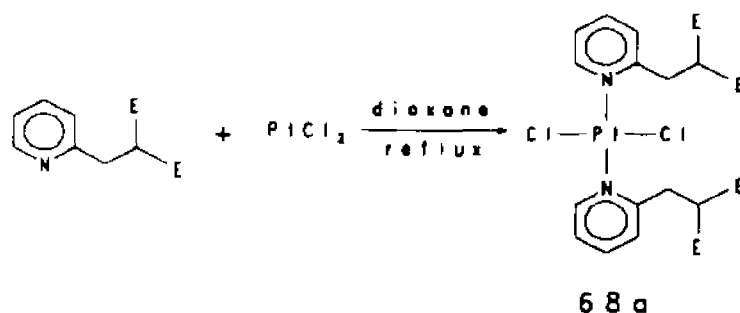
**General Comments.** All melting points were taken in open capillary tubes with either a Thomas-Hoover Unimelt or a Gallenkamp Melting Point Apparatus and are uncorrected. The  $^1\text{H}$  and  $^{13}\text{C}$  nuclear magnetic resonance spectra were recorded on a IBM/Bruker NR/80 spectrometer (80.06 and 20.08 MHz, respectively), in  $\text{CDCl}_3$  solutions, except where noted. Deuterated solvent residues were used as internal standards [ $\text{CHCl}_3$  - 7.27 ( $^1\text{H}$ ) and 77.0 ( $^{13}\text{C}$ ) ppm,  $\text{Me}_2\text{SO}$  - 2.49 ( $^1\text{H}$ ) and 39.5 ( $^{13}\text{C}$ ) ppm] and chemical shift values ( $\delta$ ) are reported in parts per million (ppm) downfield from tetramethylsilane (TMS). Infrared spectra (IR) were recorded on an IBM IR/38 Fourier transform infrared spectrophotometer. Elemental analyses were conducted by either Galbraith Laboratories, Inc. (Knoxville, TN) or M-H-W Laboratories (Phoenix, AZ). "Dry column" flash chromatography was performed by the method of

Harwood<sup>124</sup> using preparative grade silica gel (Brinkman PF-254-366) in a quartz funnel with the eluants specified.

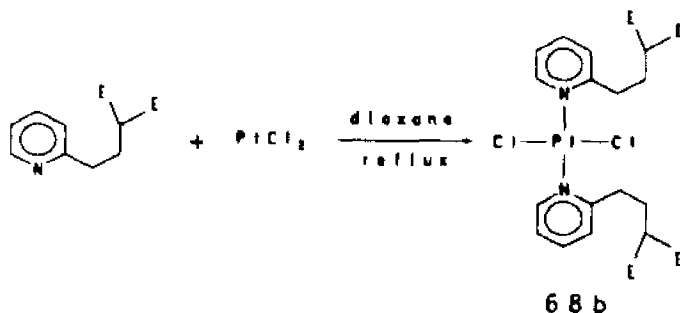
**Reagents.** Unless otherwise noted, all reagents and solvents utilized were of reagent grade and no further purification was undertaken. Methyl  $\alpha$ -(methoxycarbonyl)-[pyridine]-2-propanoate<sup>103</sup> and methyl  $\alpha$ -(methoxycarbonyl)[pyridine]-2-butanoate<sup>104</sup> were prepared by previously published procedures. Dichloroplatinum(II) and potassium tetrachloroplatinite were obtained from Engelhard Corporation.

**X-ray.** The structure determinations were carried out by Frank R. Fronczek (L. S. U.). Intensity data were collected on an Enraf-Nonius CAD4 diffractometer equipped with MoK $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) and a graphite monochromator, by  $\omega$ -2 $\theta$  scans of variable speed designed to yield equal relative precision for all significant data. A maximum was placed on the time allowed for scanning a single reflection. Crystal data and experimental details are listed in Table VII. One quadrant of data was measured for each crystal within the specified angular limits. Data reduction included corrections for background, Lorentz, polarization, and absorption by  $\psi$  scans.

Structures were solved by heavy atom methods and refined by full-matrix least squares, treating non-hydrogen atoms anisotropically. Hydrogen atoms were located by difference maps and included as fixed contributions. Final R factors and residual electron densities are given in Table VII; coordinates are listed in Tables XII, XIII, and XIV.

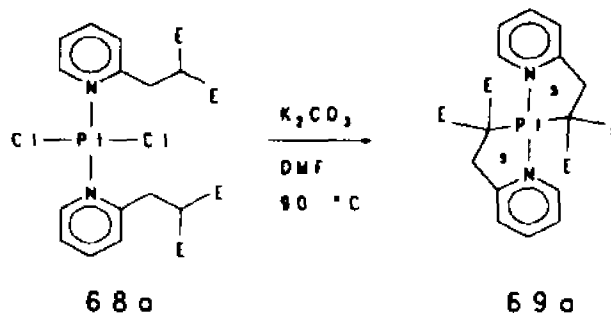


***trans*-Dichloro-bis{methyl  $\alpha$ -(methoxycarbonyl)[pyridine]-2-propanoate-*N*}platinum(II) (68a).** A stirred mixture of  $\text{PtCl}_2$  (71 mg, 267  $\mu\text{mol}$ ) and methyl  $\alpha$ -(methoxycarbonyl)[pyridine]-2-propanoate (123 mg, 552  $\mu\text{mol}$ ) in 1,4-dioxane (10 mL) was refluxed for 24 h. After cooling, the solvent was removed in vacuo and the resulting solid was triturated with  $\text{Et}_2\text{O}$  to give (70%) adduct **68a**, as a grayish white solid; 133 mg; mp 233-235  $^\circ\text{C}$ ;  $^1\text{H}$  NMR ( $\text{Me}_2\text{SO}-d_6$ )  $\delta$  3.74 (s,  $\text{OCH}_3$ , 6H), 4.20 (d,  $\text{CH}_2$ ,  $J = 7.4$  Hz, 2H), 5.12 (t,  $\text{CH}$ ,  $J = 7.4$  Hz, 1H), 7.44-7.58 (m, 3,5-pyrH, 2H), 7.93 (m, 4-pyrH, 1H), 8.88 (ds,  $^{125}\text{C}$  6-pyrH,  $J_{5,6} = 5.2$  Hz,  $J_{\text{PtH}} = 32.3$  Hz, 1H);  $^{13}\text{C}$  NMR ( $\text{Me}_2\text{SO}-d_6$ )  $\delta$  37.0 ( $\text{CH}_2$ ), 49.9 ( $\text{CH}$ ), 52.8 ( $\text{CH}_3$ ), 124.3 (C-5), 127.7 (C-3), 139.3 (C-4), 153.8 (C-6), 159.6 (C-2), 168.9 (C=O); IR (KBr) 1732vs (C=O), 1213 (C-O)  $\text{cm}^{-1}$ ; Anal. Calcd for  $\text{C}_{22}\text{H}_{26}\text{N}_2\text{Cl}_2\text{O}_8\text{Pt}$ : C, 37.09; H, 3.68; N, 3.93. Found: C, 36.91; H, 3.89; N, 3.79.



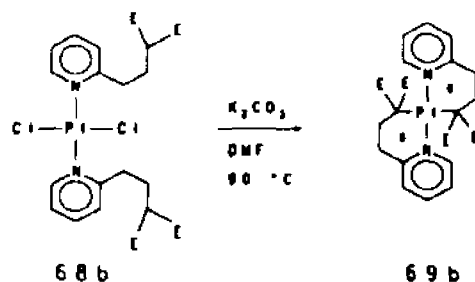
***trans*-Dichloro-bis{methyl  $\alpha$ -(methoxycarbonyl)[pyridine]-2-butanoate-*N*}platinum(II) (68b)** was similarly prepared from methyl  $\alpha$ -(methoxycarbonyl)[pyridine]-2-butanoate and  $\text{PtCl}_2$ : 83%; mp 164.2-167.0  $^\circ\text{C}$ ;  $^1\text{H}$  NMR ( $\text{Me}_2\text{SO}-d_6$ )  $\delta$  2.38-2.67 (m,  $\beta\text{-CH}_2$ , 2H), 3.71-3.96 (m,  $\alpha\text{-CH}_2$ ,  $\text{CH}$ , 3H), 3.74 (s,  $\text{CH}_3$ , 6H), 7.35-7.59 (m, 3,5-pyrH, 2H), 7.93 (ddd, 4-pyrH,  $J_{3,4} = J_{4,5} = 6.8$ ,  $J_{4,6} = 2.0$  Hz, 1H), 9.00 (ds,  $^{125}\text{C}$  6-pyrH,  $J_{5,6} = 5.1$ ,  $J_{\text{PtH}} = 26.4$  Hz, 1H);  $^{13}\text{C}$  NMR ( $\text{Me}_2\text{SO}-d_6$ )  $\delta$  27.7 ( $\beta\text{-CH}_2$ ), 36.0 ( $\alpha\text{-CH}_2$ ), 50.5 ( $\text{CH}$ ), 52.3 ( $\text{CH}_3$ ), 123.3 (C-5), 126.0 (C-3), 139.1 (C-4),

153.7 (C-6), 163.0 (C-2), 169.5 (C=O); IR (KBr) 1728vs (C=O), 1228 (C-O)  $\text{cm}^{-1}$ ; Anal. Calcd for  $\text{C}_{24}\text{H}_{30}\text{N}_2\text{Cl}_2\text{O}_8\text{Pt}$ : C, 38.93; H, 4.08; N, 3.78. Found: C, 39.07; H, 4.11; N, 3.79.

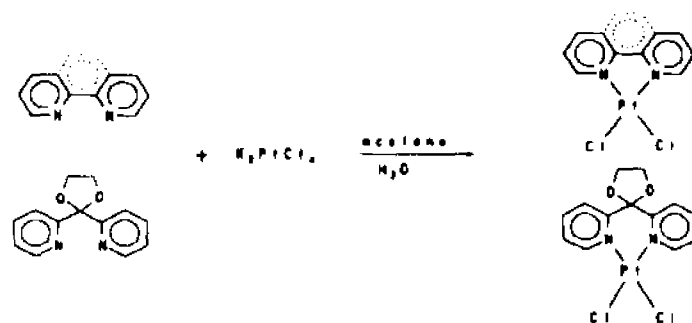


### Preparation of the C,N-chelates 69a and 69b.

**trans-Bis{methyl  $\alpha$ -(methoxycarbonyl)[pyridine]-2-propanoate-C,N}platinum-(II) (69a).** A stirred mixture of **68a** (86 mg, 121  $\mu\text{mol}$ ) and excess anhydrous  $\text{K}_2\text{CO}_3$  in DMF was heated to 90  $^{\circ}\text{C}$  and stirred for 12 h after which the DMF was removed in vacuo. The remaining solid was partially dissolved in  $\text{CHCl}_3$  and then filtered through Celite. The  $\text{CHCl}_3$  was removed and the product passed through a short chromatographic column ( $\text{SiO}_2$ ,  $\text{CHCl}_3$ ) to give (84%) **69a**, as a yellow solid: 65 mg; mp 205-208  $^{\circ}\text{C}$  (dec);  $^1\text{H}$  NMR  $\delta$  3.45 (s,  $\text{CH}_3$ , 6H), 3.66 (ss, $^{125}\text{CH}_2$ ,  $J_{\text{PtH}} = 20.3$  Hz, 2H), 7.15-7.33 (m, 5-pyrH, 1H), 7.53-7.79 (m, 3,4-pyrH, 2H), 9.18 (ds, $^{125}\text{J}_{5,6} = 5.1$ ,  $J_{\text{PtH}} = 36.8$  Hz, 1H);  $^{13}\text{C}$  NMR  $\delta$  44.1 ( $\text{CH}_2$ ,  $J_{\text{PtC}} = 17.4$  Hz), 49.3 (PtC,  $J_{\text{PtC}} = 453.2$  Hz), 50.8 ( $\text{CH}_3$ ), 120.7 (C-3,  $J_{\text{PtC}} = 33.8$  Hz), 121.5 (C-5,  $J_{\text{PtC}} = 42.0$  Hz), 137.4 (C-4,  $J_{\text{PtC}} = 8.7$  Hz), 151.8 (C-6,  $J_{\text{PtC}} = 30.5$  Hz), 172.7 (C-2,  $J_{\text{PtC}} = 37.5$  Hz), 174.6 (C=O,  $J_{\text{PtC}} = 47.9$  Hz); IR (KBr) 1686vs (C=O), 1181 (C-O)  $\text{cm}^{-1}$ ; Anal. Calcd for  $\text{C}_{22}\text{H}_{24}\text{N}_2\text{O}_8\text{Pt}$ : C, 41.32; H, 3.78; N, 4.38. Found: C, 40.98; H, 4.01; N, 4.25.



***trans*-Bis{methyl  $\alpha$ -(methoxycarbonyl)[pyridine]-2-butanoate-*C,N*}platinum(II) (69b)** was similarly prepared (purification was done by dry-column flash chromatography eluting initially with  $\text{CHCl}_3$  and then with 50%  $\text{CHCl}_3/\text{MeOAc}$ ) from **68b**: 19%; mp 220-222  $^{\circ}\text{C}$  (dec);  $^1\text{H}$  NMR  $\delta$  2.12-2.30 (m,  $\alpha\text{-CH}_2$ , 2H), 2.83 (s,  $\text{CH}_3$ , 3H), 2.93-3.74 (m,  $\beta\text{-CH}_2$ , 2H), 3.29 (s,  $\text{CH}_3$ , 3H), 7.06-7.44 (m, 3,5-pyrH, 2H), 7.71 (ddd, 4-pyrH,  $J_{4,5} = J_{3,4} = 7.6$ ,  $J_{4,6} = 1.7$  Hz, 1H), 8.91 (ddds,<sup>125</sup> 6-pyrH,  $J_{5,6} = 5.8$ ,  $J_{4,6} = 1.5$ ,  $J_{3,6} = 0.7$ ,  $J_{\text{pH}} = 41.2$  Hz, 1H);  $^{13}\text{C}$  NMR  $\delta$  28.9 ( $\beta\text{-C}$ ,  $J_{\text{PtC}} = 43.5$  Hz), 41.4 (PtC,  $J_{\text{PtC}} = 448.0$  Hz), 41.8 ( $\alpha\text{-C}$ ,  $J_{\text{PtC}} = 132.0$  Hz), 49.7 ( $\text{CH}_3$ ), 50.6 ( $\text{CH}_3$ ), 122.0 (C-3,  $J_{\text{PtC}} = 49.9$  Hz), 122.5 (C-5,  $J_{\text{PtC}} = 26.4$  Hz), 137.2 (C-4,  $J_{\text{PtC}} = 9.2$  Hz), 152.3 (C-6), 163.3 (C-2,  $J_{\text{PtC}} = 10.4$  Hz), 174.5 (C=O,  $J_{\text{PtC}} = 56.3$  Hz), 176.5 (C=O,  $J_{\text{PtC}} = 63.9$  Hz); IR (KBr) 1690s (C=O), 1196 (C-O)  $\text{cm}^{-1}$ ; Anal. Calcd for  $\text{C}_{22}\text{H}_{24}\text{N}_2\text{O}_8\text{Pt}$ : C, 43.19; H, 4.23; N, 4.20. Found: C, 43.32; H, 4.41; N, 4.13.



#### Preparation of $\text{Pt}(\text{dipy})\text{Cl}_2$ , $\text{Pt}(\text{phen})\text{Cl}_2$ , and $\text{Pt}(\text{diox})\text{Cl}_2$ .

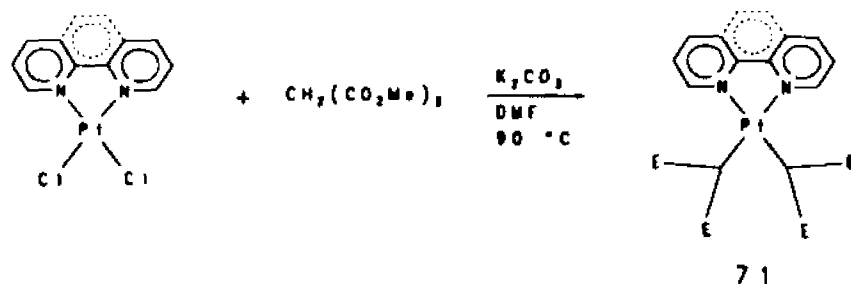
**Dichloro-2,2'-dipyridineplatinum(II).** To a stirred solution of  $\text{K}_2\text{PtCl}_4$  (960 mg,



2.31 mmol) in H<sub>2</sub>O (50 mL), 2,2'-dipyridine (377 mg, 2.42 mmol) in acetone (15 mL) was added and the temperature maintained at 65 °C for 12 h. The yellow precipitate which formed was then filtered and rinsed with H<sub>2</sub>O to give (85%) Pt(dipy)Cl<sub>2</sub>, as a yellow powder: 829 mg; mp 368-370 °C; <sup>1</sup>H NMR<sup>126</sup> (Me<sub>2</sub>SO-*d*<sub>6</sub>) δ 7.83 (dd, 5-pyrH, *J*<sub>4,5</sub> = 7.8, *J*<sub>5,6</sub> = 5.7 Hz, 1H), 8.34 (d, 3-pyrH, *J*<sub>3,4</sub> = 8.0 Hz, 1H), 8.48-8.71 (m, 4-pyrH, 1H), 9.50 (ds,<sup>125</sup> 6-pyrH, *J*<sub>5,6</sub> = 5.7, *J*<sub>PtH</sub> = 40.4 Hz, 1H); <sup>13</sup>C NMR (Me<sub>2</sub>SO-*d*<sub>6</sub> limited solubility) δ 124.2 (C-3, *J*<sub>PtC</sub> = 30.6 Hz), 127.7 (C-5, *J*<sub>PtC</sub> = 38.4 Hz), 140.5 (C-4, *J*<sub>PtC</sub> = 9.7 Hz), 148.5 (C-6, *J*<sub>PtC</sub> = 33.3 Hz) (C-2 not observed); IR (KBr) 766, 720 cm<sup>-1</sup>; Anal. Calcd for C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>Cl<sub>2</sub>Pt: C, 28.46; H, 1.91; N, 6.64. Found: C, 28.37; H, 1.70; N, 6.46.

**Dichloro-1,10-phenanthrolineplatinum(II)** was similarly prepared (86%) from 1,10-phenanthroline monohydrate and K<sub>2</sub>PtCl<sub>4</sub>: mp 400 °C; <sup>1</sup>H NMR (Me<sub>2</sub>SO-*d*<sub>6</sub>) δ 8.17 (dd, 3-phenH, *J*<sub>3,4</sub> = 8.2, *J*<sub>2,3</sub> = 5.5 Hz, 1H), 8.29 (s, 5-phenH, 1H), 9.04 (dd, 4-phenH, *J*<sub>3,4</sub> = 8.2, *J*<sub>2,4</sub> = 1.3 Hz, 1H), 9.71 (dds,<sup>125</sup> 2-phenH, *J*<sub>2,3</sub> = 5.5, *J*<sub>2,4</sub> = 1.3, *J*<sub>PtH</sub> = 41.3 Hz, 1H); IR (KBr) 839, 708 cm<sup>-1</sup>; Anal. Calcd for C<sub>12</sub>H<sub>8</sub>N<sub>2</sub>Cl<sub>2</sub>Pt: C, 32.31; H, 1.81; N, 6.28. Found: C, 32.48; H, 1.80; N, 6.24.

**Dichloro[1,1-bis(2-pyridyl)-1,3-dioxolane]platinum(II)** was similarly prepared (52%) from [1,1-bis(2-pyridyl)-1,3-dioxolane] and K<sub>2</sub>PtCl<sub>4</sub>: mp 313-315 °C (dec); <sup>1</sup>H NMR δ 4.25-4.45 (m, CH<sub>2</sub>, 2H), 7.40 (ddd, 5-pyrH, *J*<sub>4,5</sub> = 5.9, *J*<sub>5,6</sub> = 5.6, *J*<sub>3,5</sub> = 3.3 Hz, 1H), 7.79-8.04 (m, 3,4-pyrH, 2H), 9.37 (ds,<sup>125</sup> 6-pyrH, *J*<sub>5,6</sub> = 5.6, *J*<sub>PtH</sub> = 46.6 Hz, 1H); IR (KBr) 1090 cm<sup>-1</sup> (C-O); Anal. Calcd for C<sub>13</sub>H<sub>12</sub>N<sub>2</sub>Cl<sub>2</sub>O<sub>8</sub>Pt: C, 31.60; H, 2.45; N, 5.67. Found: C, 31.96; H, 2.17; N, 5.59.



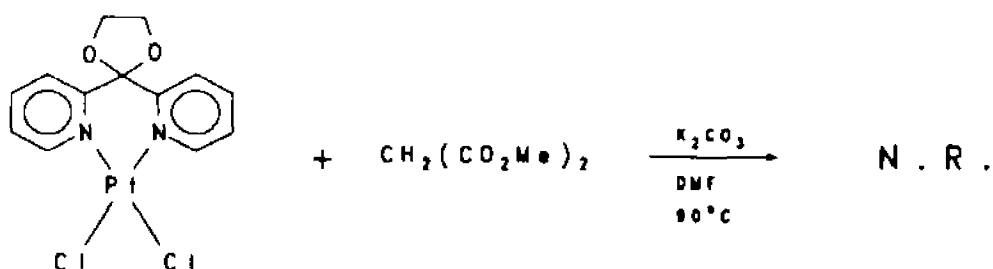
**Preparation of the *N,N'*-chelated *C*-malonato complexes **71a** and **71b**.**

**bis(Dimethyl malonato-*C*)-2,2'-dipyridineplatinum(II) (**71a**).** *Method A.* A stirred mixture of Pt(dipy)Cl<sub>2</sub> (90 mg, 213 μmol), dimethyl malonate (140 mg, 1.06 mmol), and anhydrous K<sub>2</sub>CO<sub>3</sub> (293 mg, 2.13 mmol) was kept at 90 °C for 18 h. The DMF and excess malonate were then removed in vacuo and the resulting solid triturated with CHCl<sub>3</sub>. After removing the CHCl<sub>3</sub> the product was purified on a silica gel column eluting first with CHCl<sub>3</sub> and then with MeOAc to obtain (78%) **71a**, as a bright yellow solid.

*Method B.* A stirred solution of Pt(dipy)Cl<sub>2</sub> (573 mg, 1.36 mmol) and KI (1.38 g, 8.31 mmol) in DMF (5 mL) was heated to 100 °C for 5 min. After cooling to 40 °C, dimethyl malonate (895 mg, 6.78 mmol) and anhydrous K<sub>2</sub>CO<sub>3</sub> (1.00 g, 5.68 mmol) were added and the mixture was stirred for 24h at 40 °C. The same work-up as in *Method A* above yielded (74%) **71a**: *Method A*: 102 mg; *Method B*: 617 mg; mp 210-214 °C (dec); <sup>1</sup>H NMR δ 3.62 (ss, <sup>125</sup>CH<sub>3</sub>, *J*<sub>PtH</sub> = 3.0 Hz, 6H), 4.68 (ss, <sup>125</sup>CH, *J*<sub>PtH</sub> = 129.4 Hz, 1H), 7.61 (ddd, 5-pyrH, *J*<sub>5,6</sub> = *J*<sub>4,5</sub> = 6.1, *J*<sub>3,5</sub> = 2.8 Hz, 1H), 7.99-8.19 (m, 3,4-pyrH, 2H), 10.09 (ds, <sup>125</sup>6-pyrH, *J*<sub>5,6</sub> = 6.1, *J*<sub>PtH</sub> = 25.6 Hz, 1H); <sup>13</sup>C NMR δ 19.7 (CH, *J*<sub>PtC</sub> = 635 Hz), 51.5 (CH<sub>3</sub>), 122.5 (C-3, *J*<sub>PtC</sub> = 18.2 Hz), 127.6 (C-5, *J*<sub>PtC</sub> = 27.9 Hz), 138.9 (C-4, *J*<sub>PtC</sub> = 6.5 Hz), 153.8 (C-6, *J*<sub>PtC</sub> = 32.2 Hz), 157.0 (C-2), 177.0 (C=O); IR (KBR) 1744vs, 1721s (C=O), 1136m (C-O), 783, 729

cm<sup>-1</sup>; Anal. Calcd for C<sub>22</sub>H<sub>22</sub>N<sub>2</sub>O<sub>8</sub>Pt: C, 39.16; H, 3.62; N, 4.57. Found: C, 38.95; H, 3.75; N 4.26.

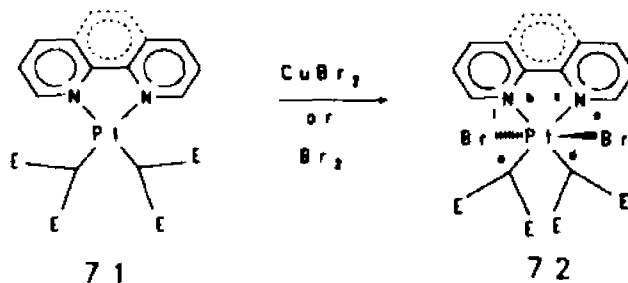
**bis(Dimethyl malonato-C)-1,10-phenanthrolineplatinum(II) (71b)** was prepared by both methods from Pt(phen)Cl<sub>2</sub>: *Method A*: 76%; *Method B*: 80%; mp 255.9-256.9 °C (dec); <sup>1</sup>H NMR δ 3.64 (ss, <sup>125</sup>CH<sub>3</sub>, J<sub>PtH</sub> = 3.4 Hz, 6H), 4.81 (ss, <sup>125</sup>CH, J<sub>PtH</sub> = 129.9 Hz, 1H), 7.89 (s, 5-phenH, 1H), 7.93 (dd, 3-phenH, J<sub>3,4</sub> = 8.2, J<sub>2,3</sub> = 5.4 Hz, 1H), 8.53 (dd, 4-phenH, J<sub>2,4</sub> = 1.4, J<sub>3,4</sub> = 8.2 Hz, 1H), 10.44 (dds, <sup>125</sup>2-phenH, J<sub>2,3</sub> = 5.4, J<sub>2,4</sub> = 1.4, J<sub>PtH</sub> = 25.6 Hz, 1H); <sup>13</sup>C NMR δ 18.8 (CH, J<sub>PtC</sub> = 634 Hz), 50.7 (CH<sub>3</sub>), 125.4 (C-3, J<sub>PtC</sub> = 29 Hz), 126.9 (C-5), 129.6 (C-4a), 137.5 (C-4), 147.0 (C-10a), 152.9 (C-2, J<sub>PtC</sub> = 34 Hz), 176.2 (C=O, J<sub>PtC</sub> = 64 Hz); IR (KBR) 1725 vs (C=O), 1138 (C-O), 841, 716 cm<sup>-1</sup>; Anal. Calcd for C<sub>22</sub>H<sub>22</sub>N<sub>2</sub>O<sub>8</sub>Pt: C, 41.45; H, 3.48; N, 4.39. Found: C, 41.36; H, 3.42; N, 4.22.



**Attempt to synthesize bis(dimethyl malonato-C)-[1,1-bis(2-pyridyl)-1,3-dioxolane]platinum(II).** To a stirred solution of dichloro[1,1-bis(2-pyridyl)-1,3-dioxolane]platinum(II) (81 mg, 160 μmol) in DMF (20 mL) was added excess dimethyl malonate and K<sub>2</sub>CO<sub>3</sub>. The mixture was heated for 20 h at 90 °C, cooled, filtered and the solvent removed in vacuo. The resulting yellow solid was then extracted with CHCl<sub>3</sub> and the CHCl<sub>3</sub> removed in vacuo. Attempted purification on a short silica gel column gave no fraction which resembled the expected product as determined by <sup>1</sup>H NMR.



**Reaction of Pt(phen)(dmm)<sub>2</sub> (71b) with methyl vinyl ketone.** After stirring a mixture of Pt(phen)(dmm)<sub>2</sub> (71b) (50 mg, 80 μmol) and methyl vinyl ketone (97 mg, 1.4 mmol) in CHCl<sub>3</sub> (25 mL) at 30 °C for 12 h, the CHCl<sub>3</sub> was removed to give unchanged Pt(phen)(dmm)<sub>2</sub> (71b) as determined by <sup>1</sup>H NMR.



#### Preparation of the dibromo Pt(IV) complexes 72a and 72b.

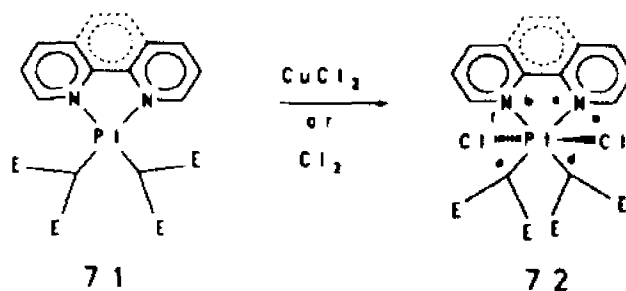
***af*-Dibromo-*de*-bis(dimethyl malonato-*C*)-*bc*-2,2'-dipyridineplatinum(IV) (72a).**

**Method A.** A 4% solution of bromine in CHCl<sub>3</sub> was added dropwise to a stirred solution of 71a (169 mg, 276 μmol) in CHCl<sub>3</sub> (5 mL) until no further color change was noted (initially the solution got lighter then suddenly turned dark from excess Br<sub>2</sub>). The excess Br<sub>2</sub> and solvent were then removed in vacuo to give (98%) the oxidized product 72a.

**Method B.** A mixture of cupric bromide (70 mg, 313 μmol) and 71a (49 mg, 80 μmol) in acetone (20 mL) was stirred at 25 °C for 12 h. The acetone was evaporated and the residue redissolved in CH<sub>2</sub>Cl<sub>2</sub> which was then filtered to remove Cu salts. Removal of the CH<sub>2</sub>Cl<sub>2</sub> in vacuo gave (73%) 72a, as a light yellow solid: **Method A:** 209 mg; **Method B:** 46 mg; mp 342-346 °C; <sup>1</sup>H NMR δ 3.72 (s, CH<sub>3</sub>, 6H), 4.94 (ss, <sup>125</sup>CH, *J*<sub>PtH</sub> = 89.9 Hz, 1H), 7.59-7.77 (m, 5-pyrH, 1H), 8.02-8.29 (m, 3,4-pyrH, 2H), 10.53 (ds, <sup>125</sup>6-pyrH, *J*<sub>5,6</sub> = 6.6, *J*<sub>PtH</sub> = 14.1 Hz); <sup>13</sup>C NMR δ 21.0 (CH, *J*<sub>PtC</sub> = 556.7 Hz), 50.8 (CH<sub>3</sub>), 123.1 (C-3, *J*<sub>PtC</sub> = 12.1 Hz), 127.1 (C-5, *J*<sub>PtC</sub> = 18.1 Hz),

140.2 (C-4), 155.9 (C-6,  $J_{\text{PtC}} = 14.5$  Hz), 157.7 (C-2,  $J_{\text{PtC}} = 16.1$  Hz), 174.3 (C=O,  $J_{\text{PtC}} = 43.0$  Hz); IR (KBr) 1744vs (C=O), 1127 (C-O), 778, 732  $\text{cm}^{-1}$ ; Anal. Calcd for  $\text{C}_{20}\text{H}_{22}\text{N}_2\text{Br}_2\text{O}_8\text{Pt}$ : C, 31.07; H, 2.87; N, 3.62. Found: C, 31.42; H, 3.21; N, 3.22.

***aq*-Dibromo-*de*-bis(dimethyl malonato-*C*)-*bc*-1,10-phenanthrolineplatinum(IV) (72b)** was prepared by both methods from **71b**: *Method A*: 98%; *Method B*: 91%; mp > 350 °C;  $^1\text{H}$  NMR  $\delta$  3.76 (ss,  $^{125}\text{CH}_3$ ,  $J_{\text{PtH}} = 3.0$  Hz, 6H), 5.04 (ss,  $^{125}\text{CH}$ ,  $J_{\text{PtH}} = 90.3$  Hz, 1H), 7.96 (s, 5-phenH, 1H), 8.00 (dd, 3-phenH,  $J_{3,4} = 8.2$ ,  $J_{2,3} = 5.5$  Hz, 1H), 8.49 (dd, 4-phenH,  $J_{3,4} = 8.2$ ,  $J_{2,4} = 1.3$  Hz, 1H), 10.89 (dds,  $^{125}$  2-phenH,  $J_{2,3} = 5.5$ ,  $J_{2,4} = 1.3$  Hz,  $J_{\text{PtH}} = 15.4$  Hz, 1H);  $^{13}\text{C}$  NMR  $\delta$  21.1 (CH,  $J_{\text{PtC}} = 560$  Hz), 50.8 ( $\text{CH}_3$ ), 126.4 (C-3,  $J_{\text{PtC}} = 18.6$  Hz), 127.5 (C-5), 131.0 (C-4a), 139.0 (C-4), 146.0 (C-10a), 156.0 (C-2,  $J_{\text{PtC}} = 15.0$  Hz), 174.5 (C=O,  $J_{\text{PtC}} = 44.3$  Hz); IR (KBr) 1746s (C=O), 1144s (C-O), 845, 716  $\text{cm}^{-1}$ ; Anal. Calcd for  $\text{C}_{22}\text{H}_{22}\text{N}_2\text{Br}_2\text{O}_8\text{Pt}$ : C, 33.14; H, 2.78; N, 3.51. Found: C, 33.35; H, 2.48; N, 3.42.



#### Preparation of the dichloro Pt(IV) complexes 72c and 72d.

***aq*-Dichloro-*de*-bis(dimethyl malonato-*C*)-*bc*-2,2'-dipyridineplatinum(IV) (72c).** *Method A.* A cooled (0 °C) saturated solution of chlorine in  $\text{CHCl}_3$  was added dropwise to a cooled (0 °C) stirred solution of **71a** (61 mg, 100  $\mu\text{mol}$ ) in  $\text{CHCl}_3$  until no further color change was noted. (Initially the solution got lighter and then turned

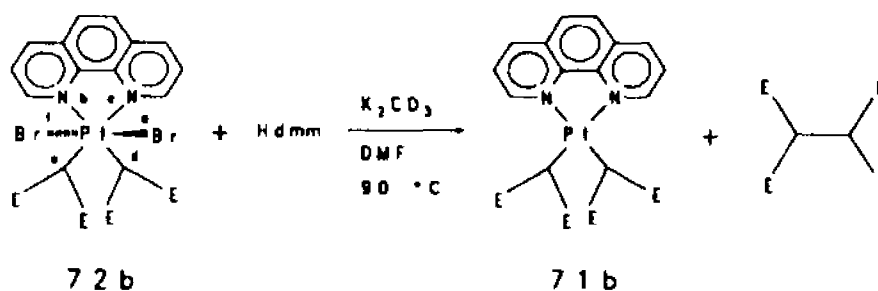
darker from excess chlorine.) The excess chlorine and  $\text{CHCl}_3$  were then removed in vacuo and the product was passed through a short silica column eluting with  $\text{CHCl}_3$  to give (56%) **72c**.

**Method B.** A mixture of **71a** (45 mg, 70  $\mu\text{mol}$ ) and  $\text{CuCl}_2$  (40 mg, 300  $\mu\text{mol}$ ) was stirred in acetone (10 mL) at 25 °C for 1 h. After filtering and removing the acetone the resulting light yellow solid was purified using flash-dry chromatography eluting initially with  $\text{CH}_2\text{Cl}_2$  and finally with 3% EtOH/ $\text{CH}_2\text{Cl}_2$  to give (83%) **72c**, as a light yellow solid: **Method A**: 38 mg; **Method B**: 42 mg; mp > 390 °C (dec);  $^1\text{H}$  NMR  $\delta$  3.72 (s,  $\text{CH}_3$ , 6H), 4.93 (ss,  $^{125}\text{CH}$ ,  $J_{\text{PtH}} = 89.1$  Hz, 1H), 7.60-7.78 (m, 5-pyrH, 1H), 7.91-8.18 (m, 3,4-pyrH, 2H), 10.53 (ds,  $^{125}$  6-pyrH,  $J_{5,6} = 6.5$ ,  $J_{\text{PtH}} = 12.8$  Hz, 1H);  $^{13}\text{C}$  NMR  $\delta$  21.0 ( $\text{CH}$ ,  $J_{\text{PtC}} = 556.5$  Hz), 50.9 ( $\text{CH}_3$ ), 123.0 (C-3,  $J_{\text{PtC}} = 12.2$  Hz), 127.1 (C-5,  $J_{\text{PtC}} = 18.0$  Hz), 140.2 (C-4), 155.2 (C-2), 156.0 (C-6,  $J_{\text{PtC}} = 14.3$ ), 174.4 (C=O); IR (KBr) 1740vs (C=O), 1127m (C-O), 762, 727  $\text{cm}^{-1}$ ; Anal. Calcd for  $\text{C}_{20}\text{H}_{22}\text{N}_2\text{Cl}_2\text{O}_8\text{Pt}$ : C, 35.10; H, 3.24; N, 4.09. Found: C, 34.90; H, 3.50; N, 4.06.

**af-Dichloro-de-bis(dimethyl malonato-C)-bc-1,10-phenanthroline(IV) (72d)** was prepared by both methods from **71b**. **Method A**: 59%; **Method B**: 69%; mp > 300 °C;  $^1\text{H}$  NMR  $\delta$  3.73 (ss,  $^{125}\text{CH}_3$ ,  $J_{\text{PtH}} = 2.7$  Hz, 6H), 5.09 (ss,  $^{125}\text{CH}$ ,  $J_{\text{PtH}} = 88.7$  Hz, 1H), 7.95 (s, 5-phenH, 1H), 8.01 (dd, 3-phenH,  $J_{3,4} = 8.2$ ,  $J_{2,3} = 5.5$  Hz, 1H), 8.50 (dd, 4-phenH,  $J_{3,4} = 8.2$ ,  $J_{2,4} = 1.3$  Hz, 1H), 10.88 (ds,  $^{125}$  2-phenH,  $J_{2,3} = 5.5$ ,  $J_{\text{PtH}} = 14.6$  Hz, 1H);  $^{13}\text{C}$  NMR  $\delta$  23.9 ( $\text{CH}$ ,  $J_{\text{PtC}} = 560.6$  Hz), 50.9 ( $\text{CH}_3$ ), 125.9 (C-3,  $J_{\text{PtC}} = 18.3$  Hz), 127.5 (C-5), 131.0 (C-4a), 139.1 (C-4), 155.5 (C-2,  $J_{\text{PtC}} = 14.0$  Hz), 173.8 (C=O); IR (KBr) 1744 (C=O), 1129 (C-O), 847, 718  $\text{cm}^{-1}$ ; Anal. Calcd for  $\text{C}_{22}\text{H}_{22}\text{N}_2\text{Cl}_2\text{O}_8\text{Pt}$ : C, 37.30; H, 3.13; N, 3.95. Found: C, 37.42; H, 3.22, N, 3.76.

When **Method B** was used with **71b**, the cis complex **73** was also isolated:

**cis(Dichloro)-bis(dimethyl malonato-C)-1,10-phenanthrolineplatinum(IV) (73):** 5%; mp >260 °C;  $^1\text{H}$  NMR  $\delta$  2.56 (ss,  $^{125}\text{CH}_3$ ,  $J_{\text{PtH}} = 2.2$  Hz, 3H), 3.58 (ss,  $^{125}\text{CH}_3$ ,  $J_{\text{PtH}} = 2.5$  Hz, 3H), 3.73 (s,  $\text{CH}_3$ ,  $J_{\text{PtH}} = 2.2$  Hz, 3H), 3.84 (s,  $\text{CH}_3$ ,  $J_{\text{PtH}} = 2.2$  Hz, 3H), 4.52 (ss,  $^{125}\text{CH}$ ,  $J_{\text{PtH}} = 85.6$  Hz, 1H), 5.88 (ss,  $^{125}\text{CH}$ ,  $J_{\text{PtH}} = 98.9$  Hz, 1H), 7.92-8.16 (m, 3,5,6,8-phenH, 4H), 8.59 (dd, 7-phenH,  $J_{7,8} = 8.2$ ,  $J_{7,9} = 1.2$  Hz, 1H), 8.63 (dd, 4-phenH,  $J_{3,4} = 8.3$ ,  $J_{2,4} = 1.3$  Hz, 1H), 9.60 (dds,  $^{125}$  2-phenH,  $J_{2,3} = 5.4$ ,  $J_{2,4} = 1.3$ ,  $J_{\text{PtH}} = 14.9$  Hz, 1H), 10.86 (dds,  $^{125}$  9-phenH,  $J_{8,9} = 5.7$ ,  $J_{7,9} = 1.2$ ,  $J_{\text{PtH}} = 30.4$  Hz, 1H); (insufficient sample for CHN analysis).

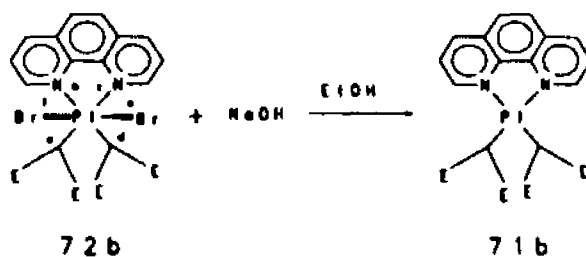


**Attempt to synthesize Pt(phen)(dmm)<sub>4</sub> (74).** Dimethyl malonate (80 mg, 610  $\mu\text{mol}$ ) and anhydrous  $\text{K}_2\text{CO}_3$  (134 mg, 970  $\mu\text{mol}$ ) were added to a solution of freshly prepared  $\text{Pt(phen)(dmm)}_2\text{Br}_2$  (**72b**) (75 mg, 90  $\mu\text{mol}$ ) in DMF (10 mL) and the solution was heated to 90 °C for 12 h. The DMF and excess malonate were then removed in vacuo and the remaining solid triturated with  $\text{CHCl}_3$ . After filtration and removal of the  $\text{CHCl}_3$  the product was purified by flash-dry chromatography eluting first with  $\text{CHCl}_3$  and then with 30% MeOAc/ $\text{CHCl}_3$ .

The  $\text{CHCl}_3$  fraction afforded (88%) **dimethyl 2,3-bis(methoxycarbonyl)butandioate**,<sup>127</sup> as determined by  $^1\text{H}$  NMR: 22 mg.

The MeOAc/ $\text{CHCl}_3$  fraction afforded (77%) **bis(dimethyl malonato-C)-1,10-phenanthrolineplatinum(II) (71b)**: 47 mg.



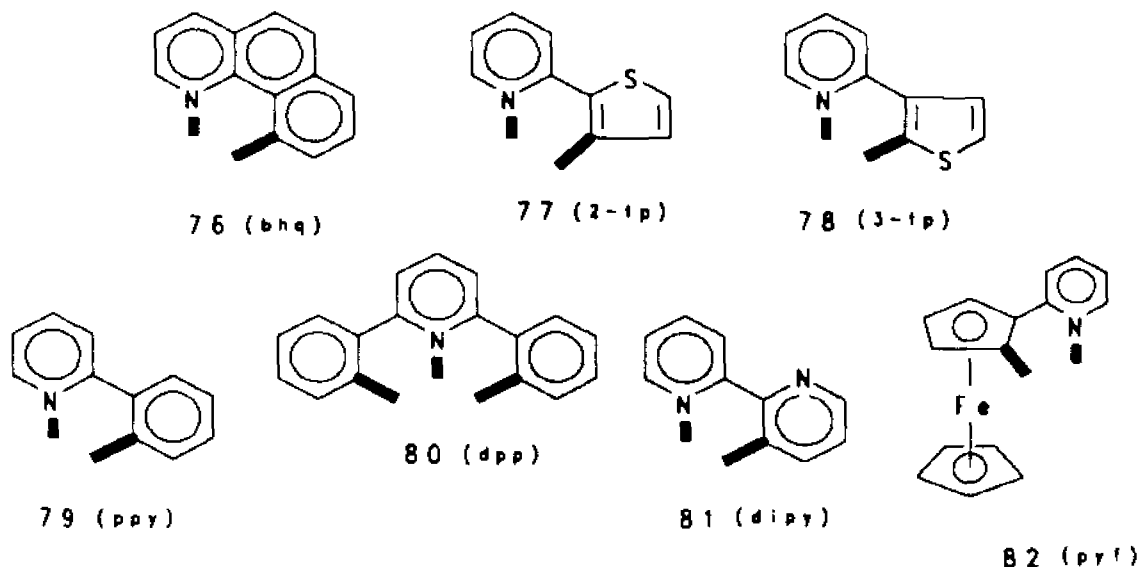


**Reaction of Pt(phen)(dmm)<sub>2</sub>Br<sub>2</sub> (72b) with NaOH.** Pt(phen)(dmm)<sub>2</sub>Br<sub>2</sub> (**72b**) (40 mg, 50  $\mu$ mol) in CH<sub>2</sub>Cl<sub>2</sub> (5 mL) was added to a solution of NaOH (52 mg, 1.3 mmol) in EtOH (5 mL). The mixture was stirred for 15 min at 25 °C. More CH<sub>2</sub>Cl<sub>2</sub> was added and the solution washed twice with aqueous saturated NaCl. The CH<sub>2</sub>Cl<sub>2</sub> solution was then dried over anhydrous MgSO<sub>4</sub> and the solvent removed to give Pt(phen)(dmm)<sub>2</sub> (**71b**), as a yellow solid (8 mg, 25%).

## Chapter 2.      Cyclopalladated Complexes of 2-Vinylpyridine Derivatives Possessing Pd-C<sub>sp</sub><sup>2</sup> Bonds

### Introduction

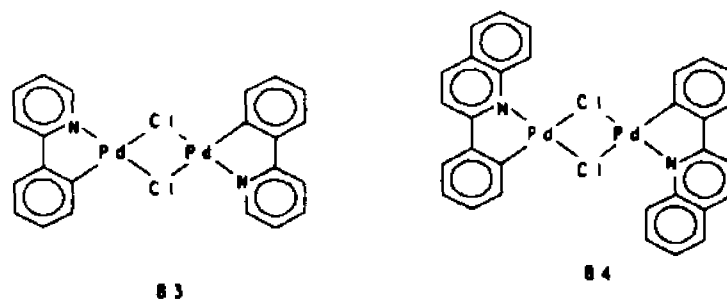
Although *N,C*-cyclometalated sigma complexes, in which the carbon bonded to the metal is sp<sup>2</sup> hybridized, are well known, examples of complexes where the *N*-donor is pyridine are rather limited.<sup>128</sup> Most reports have used one of the following ligands where the metalated carbon is part of an aromatic ring: benzo-*[h]*-quinolines (bhq, **76**), 2-(2'-thienyl)pyridines (2-tp, **77**), 2-(3'-thienyl)pyridines (3-tp, **78**), 2-phenylpyridines (ppy, **79**), 2,6-diphenylpyridines (dpp, **80**), 2,2'-dipyridines (dipy, **81**), and 2-pyridinylferrocenes (pyf, **82**). For comparison purposes, this discussion will be limited to those complexes that contain only carbon non-ligating atoms in the chelate ring.



### History and Background

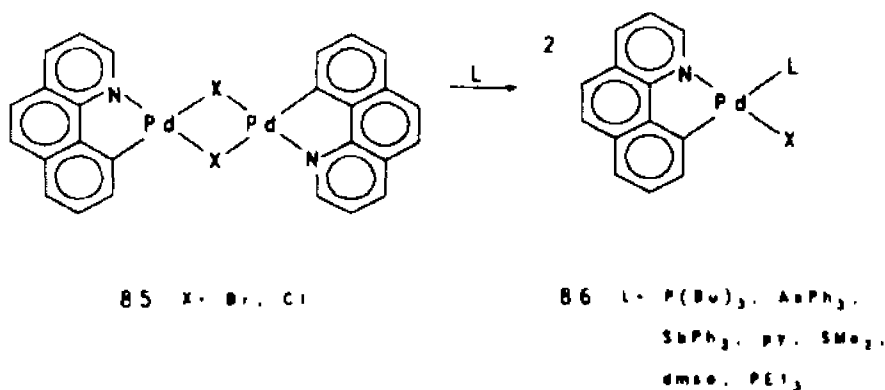
#### Palladium and Platinum Complexes

Kasahara reported<sup>129</sup> the first example of a *N,C*<sub>sp</sub><sup>2</sup> complex of a pyridine ligand in which [Pd(ppy)Cl]<sub>2</sub> (**83**) was synthesized. In support of this structure, **83** was treated with LiAlD<sub>4</sub> to give 2-phenylpyridine-*d*<sub>1</sub> in which the deuterium was located

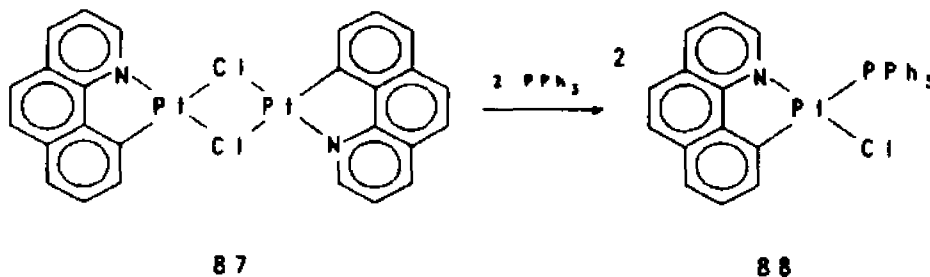


at the 2-position of the phenyl ring as determined by mass spectroscopy. Complex **84** was also reported<sup>129</sup> and treated with  $\text{LiAlD}_4$  in an analogous manner.

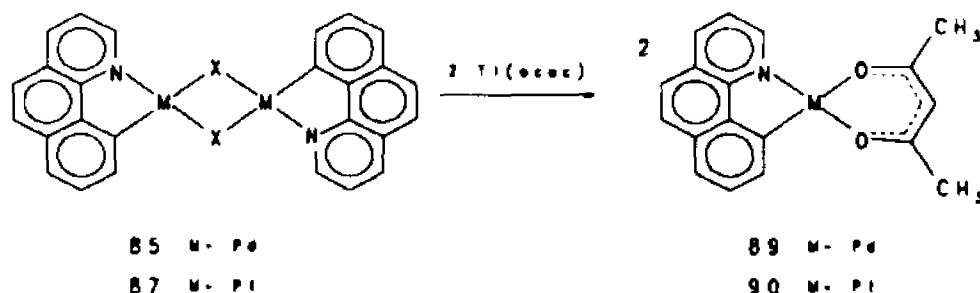
The related ligand, benzo-[h]-quinoline, was also found<sup>130</sup> to cyclometalate with  $\text{K}_2\text{PdX}_4$  ( $\text{X} = \text{Cl}, \text{Br}$ ) to form  $[\text{Pd}(\text{bhq})\text{X}]_2$  (**85**). A far IR and Raman spectroscopic study was conducted in order to assign the bridged M-X frequencies.<sup>131</sup> When dimer **85** was treated with various ligands, the monomeric  $\text{PdX}(\text{bhq})\text{L}$ <sup>130,132,133</sup> (**86**) were isolated. The corresponding Pt(II) complexes have also been reported.<sup>132</sup>



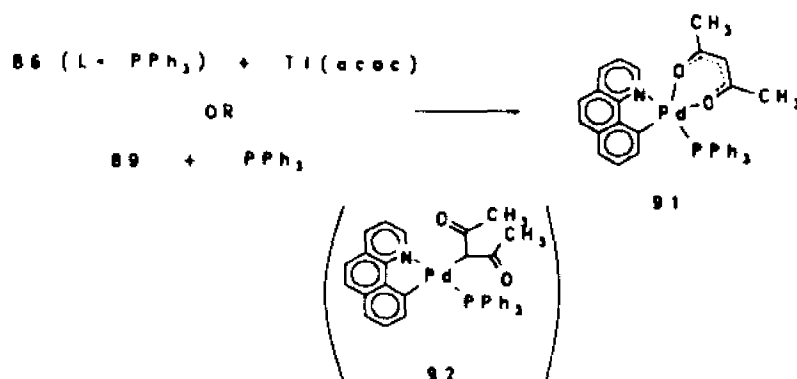
Cockburn et al. synthesized<sup>134</sup>  $[\text{Pt}(\text{bhq})\text{Cl}]_2$  (**87**), then studied the chemistry of both



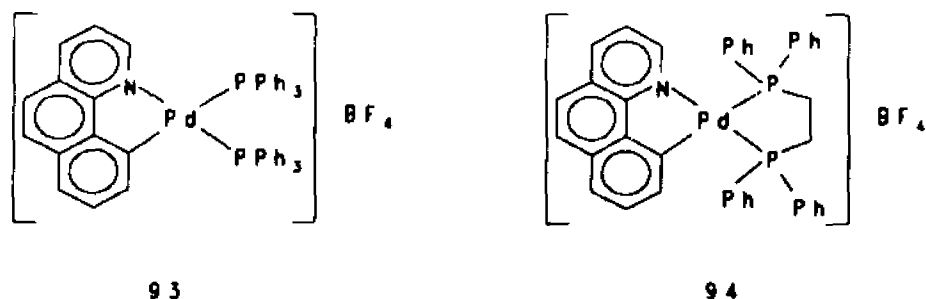
**85** and **87** with respect to dimer cleavage, metathesis, and salt formation. Thus, when **87** was reacted with  $\text{PPh}_3$ , the monomer  $\text{Pt}(\text{bhq})(\text{PPh}_3)\text{Cl}$  (**88**) was obtained. When **85** or **87** was treated with  $\text{Ti}(\text{acac})$ , the  $O,O'$ -chelated monomer **89** or **90**, respectively, were obtained.  $^{13}\text{C}$  NMR spectroscopy of **89** and the related  $\text{Pd}(\text{bhq})\text{cp}$  were reported<sup>135</sup> but complete assignments have not yet been reported. When **89** was treated



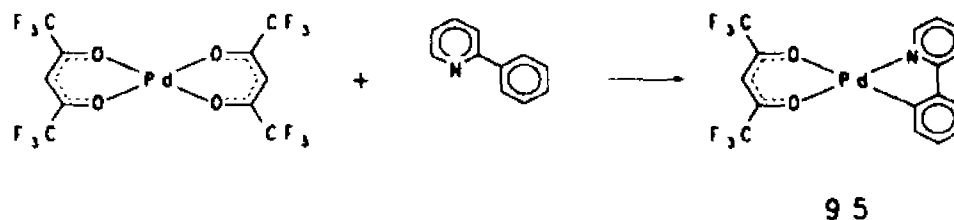
with  $\text{PPh}_3$ , or **86** ( $\text{L} = \text{PPh}_3$ ) was treated with  $\text{Ti}(\text{acac})$ ,  $\text{Pd}(\text{bhq})(\text{acac})\text{PPh}_3$  (**91**) was obtained. The authors proposed a penta-coordinate  $O,O'$ -chelate, as the structure; however,  $O,O'$ -chelates are known to rearrange to central-C bonded complexes upon addition of certain ligands<sup>14,15,18,27,59,61,62,67</sup>, thus **92** is the probable structure of



$\text{Pd}(\text{bhq})(\text{acac})\text{PPh}_3$ . No IR data were given which would differentiate between **91** and **92**. The ionic complexes  $[\text{Pd}(\text{bhq})(\text{PPh}_3)_2][\text{BF}_4]$  (**93**) and  $[\text{Pd}(\text{bhq})(\text{diphos})][\text{BF}_4]$  (**94**) were also prepared.



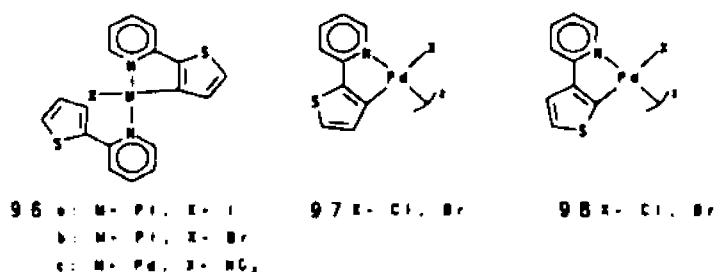
Siedle has shown<sup>60</sup> that  $\text{Pd}(\text{hfac})_2$  reacts spontaneously with Hppy to give the orthometalated  $\text{Pd}(\text{hfac})(\text{ppy})$  **95** with concomitant elimination of one of the hfac moieties. The hfac in **95** was *O,O'*-chelated as shown by its  $\text{C}=\text{O}$  absorption (IR) at  $1640\text{ cm}^{-1}$ .



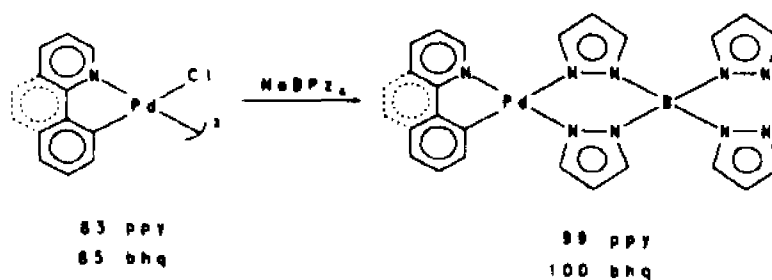
Motivated by the fact that thiophene readily undergoes metalation with certain metals, Giordano and Rasmussen investigated the metalation of 2-(2'-thienyl)pyridine with  $\text{Pd}(\text{II})$  and  $\text{Pt}(\text{II})$  and found<sup>136</sup> that, instead of *N,S*-chelation, cyclometalation occurred at ambient temperature to form **96**; an X-ray crystal structure determination of **96a** confirmed the existence of the carbon-metal bond.

The bis-cyclometalated complexes of both 2-(2'-thienyl)- (**97**) and 2-(3'-thienyl)-pyridine (**98**) were also reported.<sup>137</sup> When **97** or **98** was reacted with either py or  $\text{PBU}_3$ , the monomeric cyclometalated complexes were generated and characterized by the IR and  $^1\text{H}$  NMR data.

An interesting metathetical reaction has been reported<sup>138</sup> in which  $[\text{Pd}(\text{C}\sim\text{N})\text{Cl}]_2$  (**83** or **85**) was treated with sodium tetrakis(1-pyrazolyl)borate ( $\text{NaBPz}_4$ ), to give the

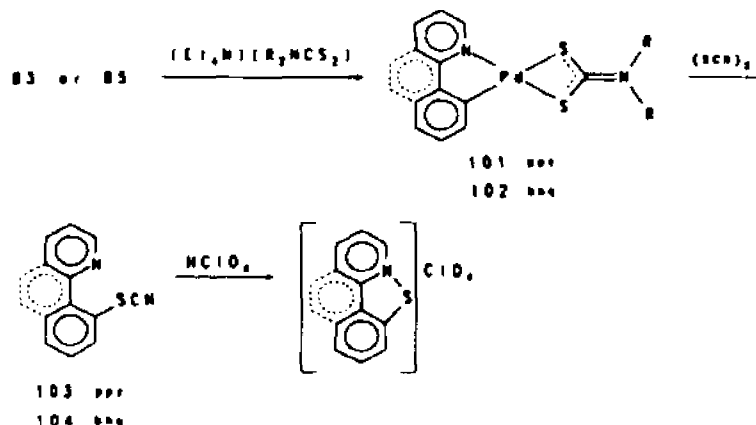


monomeric Pd(C-N)(BPz<sub>4</sub>) (**99** or **100**, respectively) was isolated. The <sup>1</sup>H NMR spectra of the products indicated that the pyrazolyl groups readily exchanged intramolecularly at ambient temperature.



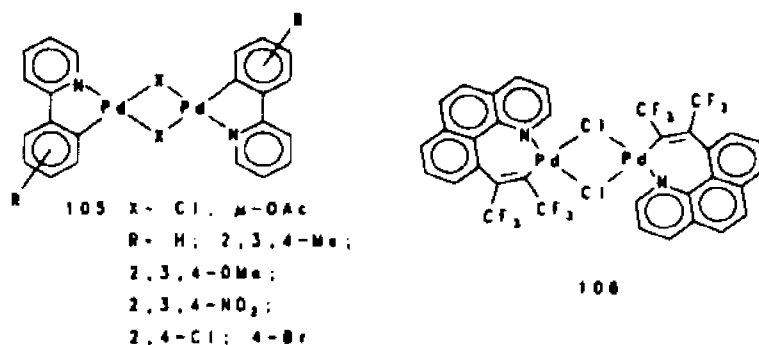
Utilization of Pd(II) cyclometalated complexes in the synthesis of *S*-heterocycles was shown by Davis et al.<sup>139</sup> whereby an initial ligand exchange on **83** or **85** (or the corresponding bridged acetates) with tetraethylammonium *N,N*-dialkyldithiocarbamate generated the monomeric **101** or **102**, respectively, which in turn reacted with thiocyanogen to give the non-metalated **103** or **104**, respectively, which was subsequently cyclized with perchloric acid to yield the corresponding isothiazolium perchlorates.

Numerous 2-phenylpyridine derivatives were used to gain insight into the mechanism of cyclopalladation of 2-phenylpyridine. Thus, complexes **105** were prepared<sup>140</sup> in which varied substitution patterns of electron-withdrawing and electron-donating groups were present and it was concluded that, after initial *N*-complexation,



the aryl ring undergoes electrophilic attack by the palladium atom leading to the cyclometalated product (**105**).

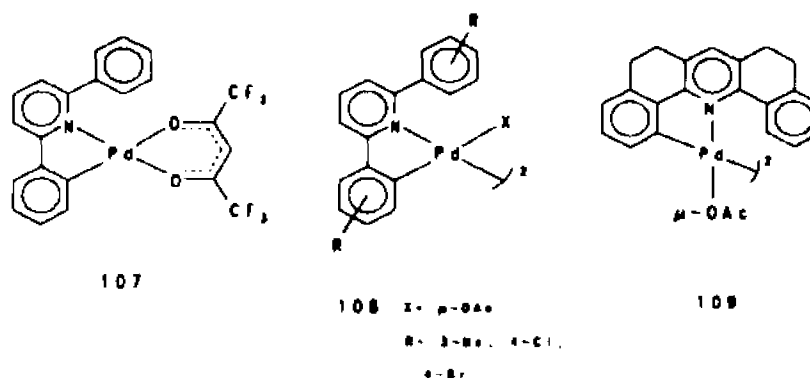
Complex **85** was found<sup>141</sup> to undergo an insertion reaction with hexafluoro-2-butyne to give dimer **106**, which contains two 7-membered chelates. The structure of **106** was deduced by elemental analysis, IR, and comparison to similar complexes whose crystal structures were determined.



The potential terdentate 2,6-diphenylpyridine (dpp) could possibly undergo cyclometalation twice to give a fused-ring complex with trans C-metal bonds similar in structure to terpyridine complexes. The first cyclometalation with dpp, however, only exhibited mono-metalation to give **107** in 80% yield from  $Pd(hfac)_2$ .<sup>59</sup>

Selbin and Gutierrez later reported<sup>142</sup> a series of diarylpyridine complexes (**108**)

in which the aryl group possessed 3-CH<sub>3</sub>, 4-Cl, or 4-Br substituent. *No bis-metalated complexes were found.* It was thought that electron-withdrawing groups in the 4-position of the phenyl rings would make the electrophilic attack of the Pd-atom on the ring facile enough to overcome any steric interaction. In addition, although dibenz[c,h]acridine did not cyclometalate, 5,6,8,9-tetrahydrodibenz[c,h]acridine did undergo *mono-metalation* to give **109** in 67% yield<sup>142</sup>. Detailed <sup>1</sup>H NMR analyses of **108** and **109** were presented.



The first example of the 2:1 bis-cyclometalated Pt(ppy)<sub>2</sub> (**110**) was reported<sup>143</sup> by Chassot and Zelewsky in 1983. And later, an X-ray crystal structure determination proved the assigned structure.<sup>144</sup> Complex **110** was also found to react with Br<sub>2</sub> to give the corresponding Pt(IV) complex Pt(ppy)<sub>2</sub>Br<sub>2</sub>. Synthesis of the related Pt(2-tp)<sub>2</sub> (**111**) and Pt(3-tp)<sub>2</sub> (**112**) were also reported<sup>145</sup> by initial lithiation of the appropriate ligand, followed by metal-metal (ligand-ligand) exchange. In this manner, only the homoleptic complexes **110–112** were obtained rather than the bridged dimers **83** (M = Pt), **97**, or **98**. Regardless of whether cis- or trans-PtCl<sub>2</sub>(SEt<sub>2</sub>)<sub>2</sub> was used as starting material, only the cis isomers **110–112** were obtained.

Studies on the interesting photochemical<sup>146–149</sup> and electrochemical<sup>150</sup> properties of this type of complex showed for example, that, in CH<sub>2</sub>Cl<sub>2</sub>, **111**, under irradiation (Hg

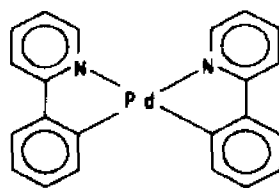


lamp), gave  $\text{Pt}(\text{2-tp})_2(\text{CH}_2\text{Cl})\text{Cl}$  (**113**) by cis photo-oxidative addition.<sup>147</sup> Several other alkyl and acyl halides were also found to react in this manner.<sup>148</sup>

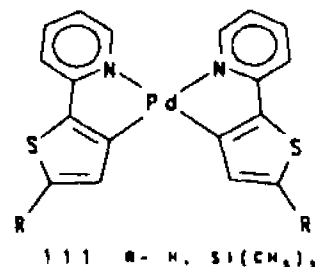
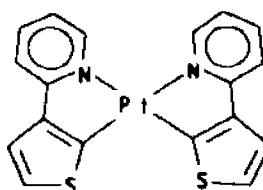
Reaction of  $[\text{Pd}(\text{bhq})\text{Cl}]_2$  (**10**) with 8-lithio-1-methoxynaphthalene gave the mixed bis-cyclometalated **114**, as a mixture of cis and trans isomers.<sup>151</sup>

Reaction of **114** with  $\text{PMe}_2\text{Ph}$

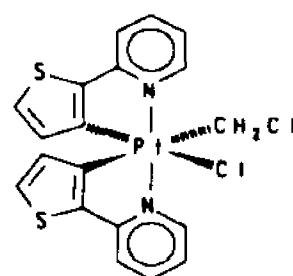
cleaved the weak Pd-O bond to give **115**; complex **114** was also found to undergo an insertion reaction with hexafluorobut-2-yne to give **116**.<sup>152</sup> The weak Pd-O bond was broken and replaced by a  $\eta^2$  bond from the naphthyl group. This was the first time that such a bond had been observed in a Pd(II) complex. The structure of a related complex was confirmed by X-ray crystallography.<sup>152</sup>



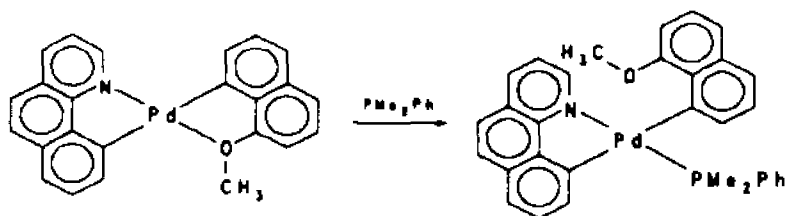
110

111 R = H, Si(CH<sub>3</sub>)<sub>3</sub>

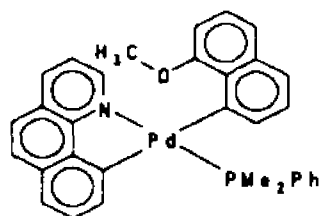
112



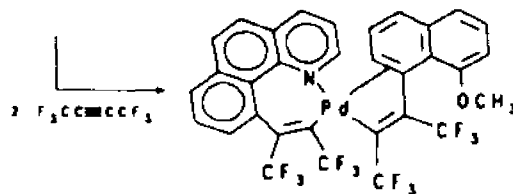
113



114

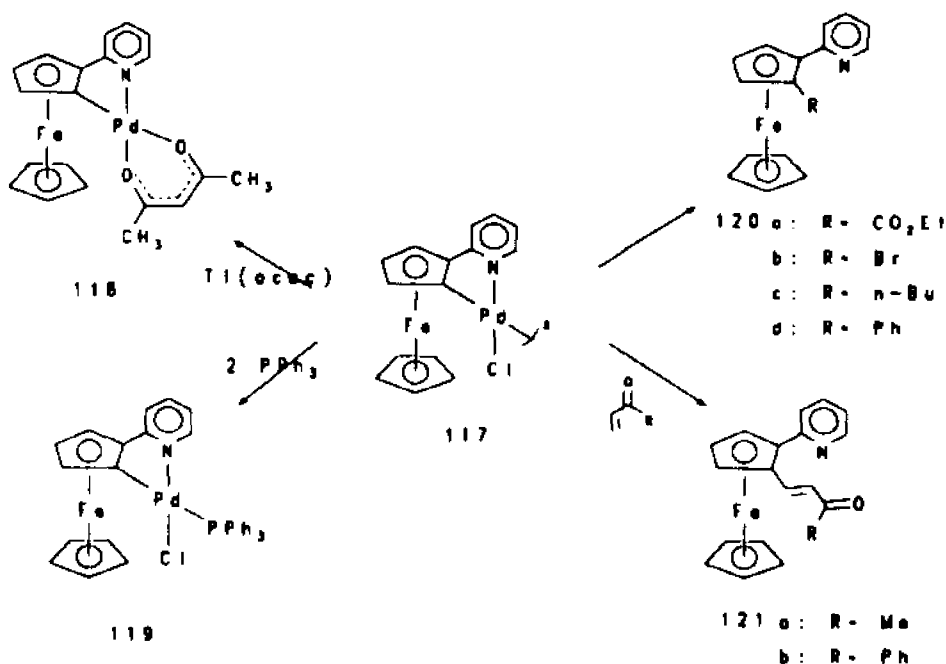


115



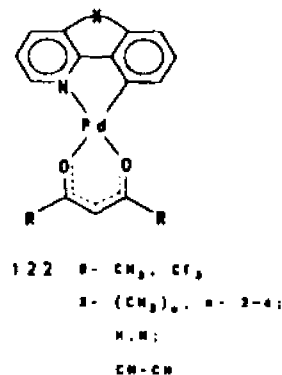
116

An interesting approach to cyclometalation based on previous reports of metallocene cyclometalation was reported<sup>153</sup> by Kasahara et al. in which 2-pyridinylferrocene (pyf) reacted with  $\text{Li}_2\text{PdCl}_4$  in the presence of NaOAc to give dimer **117**. Dimer **117** was readily cleaved by reaction with  $\text{Tl}(\text{acac})$  or  $\text{PPh}_3$  to give **118** or **119**, respectively. Reaction of **117** with  $\text{CO}/\text{EtOH}$ ,  $\text{Br}_2$ ,  $n\text{-BuLi}$ , or  $\text{PhLi}$  gave non-metallated products **120a-d**, respectively. In support of the structure of **117**,



reaction with  $\text{LiAlD}_4$  gave 1-(2-pyridinyl)ferrocene-2- $d_1$ . Complex **117**, when treated with methylvinylketone and phenylvinylketone, gave **121a** and **121b**, respectively, albeit in low yields (8 and 20%, respectively).<sup>154</sup>

Thummel and Jahng synthesized a series of bridged phenylpyridines, in which the dihedral angle between the aromatic rings was varied from 0 to  $80^\circ$ , in order to investigate the mechanism of cyclometalation.<sup>155</sup> Thus, complexes **122** were



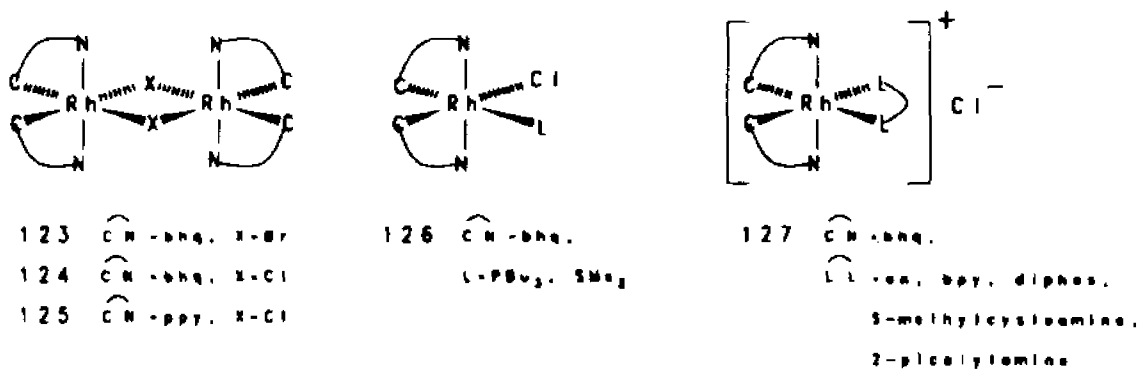
prepared and spectroscopic, kinetic, and H/D isotope effect data reported; an alternative mechanism to the electrophilic attack of the Pd-atom on the aromatic ring, an oxidative addition mechanism was put forth but, based on the reported data, no conclusion was reached.

### Ruthenium, Rhodium and Iridium Complexes

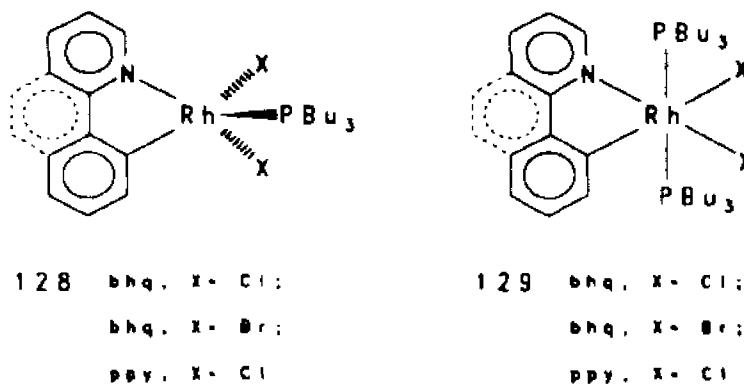
$\text{RhCl}_3 \cdot \text{H}_2\text{O}$  was found to react with Hbhq and Hppy to give the octahedral dimers  $[\text{RhX}(\text{C}-\text{N})_2]_2$  (**123**: C-N = bhq, X = Br, **124**: C-N = bhq, X = Cl; **125**: C-N = ppy, X = Cl).<sup>156</sup> Treatment of **124** with  $\text{PBU}_3$  or  $\text{SMe}_2$  gave the corresponding monomers **126**. The interesting  $^1\text{H}$  NMR spectra of **124** and **126** (L =  $\text{PBU}_3$ ) were discussed and the nitrogens of the cyclometalated ligands were proposed to be in a trans orientation based on spectroscopic evidence (IR,  $^1\text{H}$  NMR).

Later, the chemistry of **124** was investigated<sup>157</sup> and it was found to react with a variety of ligands to give monomers **126** (L = py, 4-pic,  $\text{H}_2\text{NCH}_3$ , dmsO). Reaction of **124** with NaSMe gave a neutral complex whose formula was given as  $\text{Rh}(\text{bhq})_2(\text{SMe}) \cdot 1/2 \text{H}_2\text{O}$  but no structure was assigned; NaOAc gave the neutral  $\text{Rh}(\text{bhq})_2(\text{OAc})$  in which the acetate was bidentate as determined by IR. Bidentate ligands reacted with **124** to give the corresponding charged monomers **127**, as shown by conductivity measurements. Metatheses of **124** with LiBr in  $\text{Me}_2\text{SO}$  and **126** (L =  $\text{PBU}_3$ ) with LiBr gave monomers  $\text{Rh}(\text{bhq})_2(\text{dmsO})\text{Br}$  and  $\text{Rh}(\text{bhq})_2(\text{PBU}_3)\text{Br}$ , respectively.

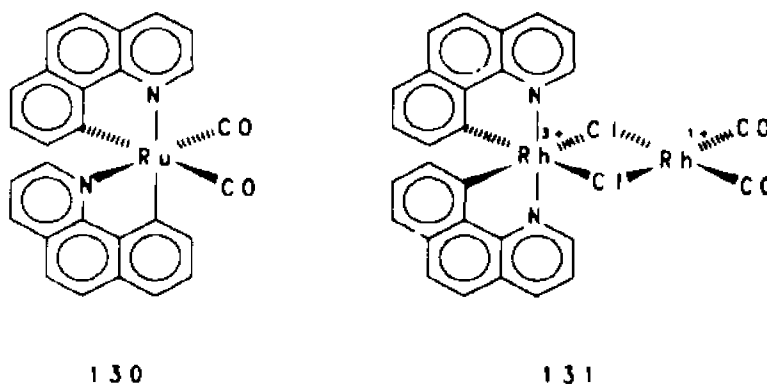
Reaction of  $[\text{RhX}_3(\text{PBU}_3)_2]_2$  with two molar equivalents of Hbhq or Hppy gave the mono-metalated penta-coordinate complexes **128**<sup>158</sup> which, when treated with one equivalent of  $\text{PBU}_3$ , gave the octahedral complexes **129**. Interestingly, reaction of



$\text{RhCl}_2(\text{bhq})(\text{PBu}_3)_2$  with NaI gave, instead of the expected di-iodo complex,  $\text{RhClI}(\text{bhq})(\text{PBu}_3)_2$ , where the iodide was trans to the metalated carbon due to the higher trans effect of the metalated C-atom compared to the heterocyclic N-atom.

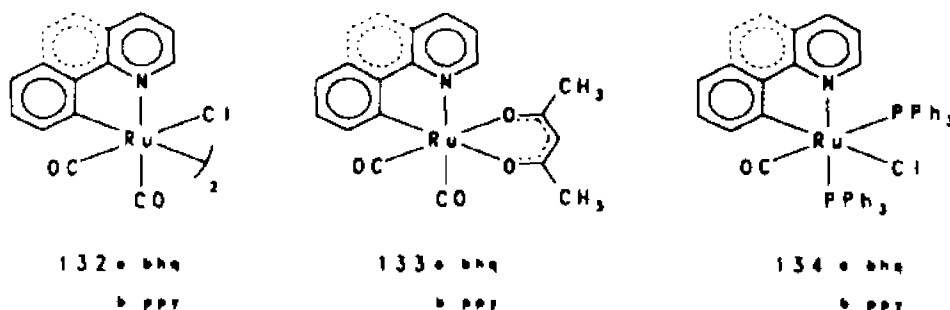


Bruce et al. first reported<sup>159</sup> the synthesis of a cyclometalated  $\text{Ru}(\text{II})$  complex with a pyridine-type ligand in 1973. The trimeric  $\text{Ru}_3(\text{CO})_{12}$  was found to react with  $\text{Hbhq}$  to form  $\text{Ru}(\text{bhq})_2(\text{CO})_2$  (**130**) in 27% yield. An X-ray crystal structure was later

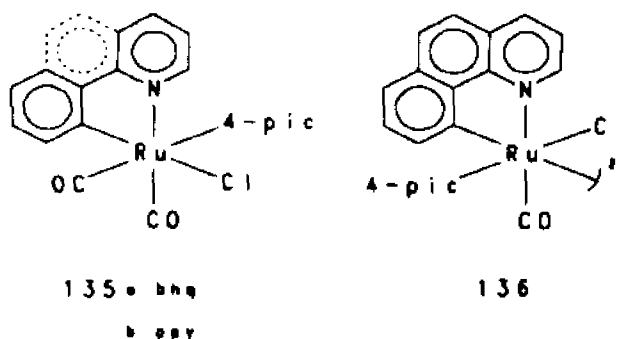


conducted<sup>160</sup> which showed the cis arrangement of the heteroatoms. In a similar manner, reaction of  $\text{Rh}(\text{CO})_2\text{Cl}$  and Hbhq gave the dinuclear complex **131** in which one Rh-atom is tri-valent and the other is mono-valent.<sup>159</sup>

The dimeric complexes  $[\text{Ru}(\text{C}\sim\text{N})(\text{CO})_2\text{Cl}]_2$  (**132**), prepared from  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$  (pre-treated with CO) and either Hbhq or Hppy, were reported<sup>161</sup> and found to undergo a number of cleavage reactions. For example, treatment of **132** with  $\text{Ti}(\text{acac})_3$  in



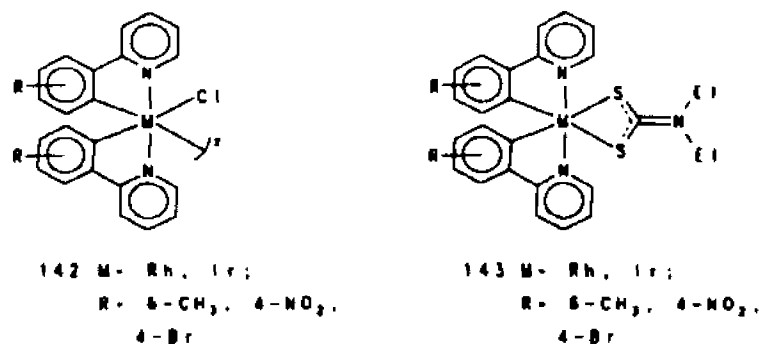
$\text{CH}_2\text{Cl}_2$  gave the *O,O'*-chelates **133** or with  $\text{PPh}_3$  gave monomers **134**. 4-Picoline reacted with **132** to give **135** but, in the case of **132a**, the dimer **136** was also obtained in 10% yield.



2-(2-Thienyl)pyridine ( $\text{H}_2\text{-tp}$ ) was found<sup>137</sup> to react with  $[\text{RuCl}_2(\text{CO})_3]_2$  to give the cyclometalated dimer **137**, which could be split by treatment with either py or  $\text{PBU}_3$  into monomers **138**. Similarly,  $[\text{RhX}_3(\text{PBU}_3)_2]_2$  reacted with  $\text{H}_2\text{-tp}$  ( $\text{X} = \text{Cl}, \text{Br}$ ) and  $\text{H}_3\text{-tp}$  ( $\text{X} = \text{Cl}$ ) to give dimers **139**.

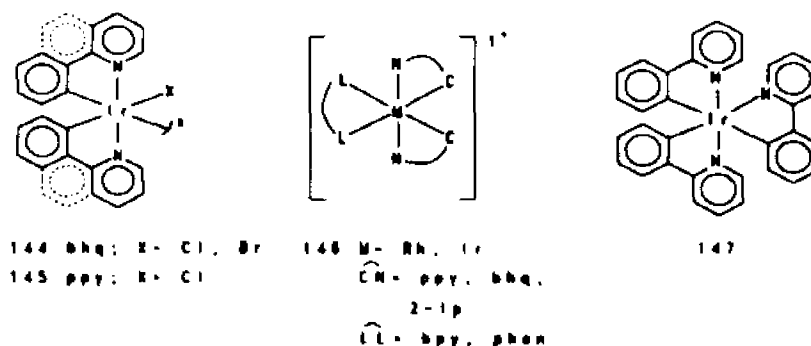
Because of its similarity to  $\text{Ru}(\text{dipy})_3$ ,<sup>2+</sup> Selbin and co-workers synthesized and





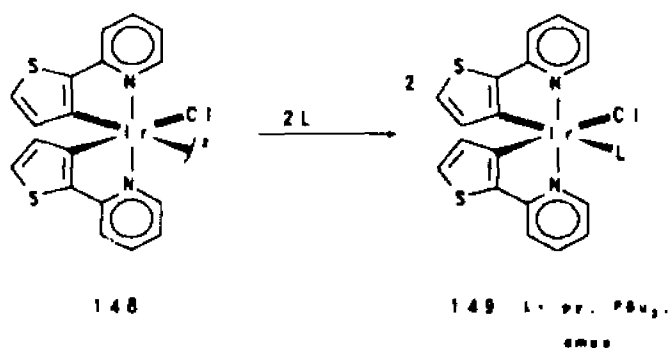
corresponding 2-phenylpyridine complexes  $[\text{Ir}(\text{ppy})_2\text{Cl}]_2$  (**145**) were synthesized<sup>167</sup> and the photophysics of **124**, **125**, **144**, and **145** was studied and correlated.

Because the metal-bound carbon and nitrogen cannot be unambiguously distinguished by X-ray structure determination, the complex  $[\text{Ir}(\text{ptpy})_2\text{Cl}]_2$  [ptpy = 2-(*p*-tolyl)pyridine] was prepared and its structure determined to show that these complexes have two mutually trans Ir-N bonds and two mutually cis Ir-C bonds.<sup>168</sup>

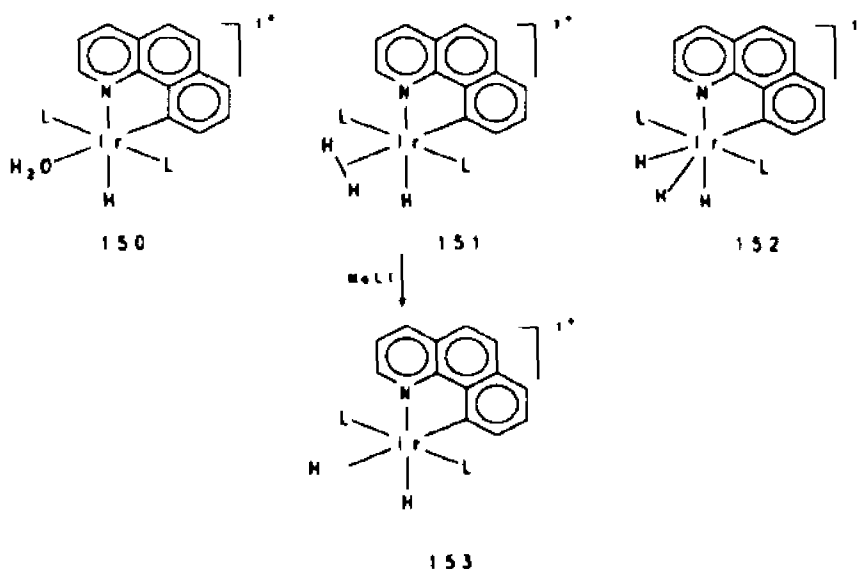


The absorption spectra, electrochemistry, luminescence, and excited state lifetimes of  $[\text{M}(\text{C}\sim\text{N})_2(\text{L}\sim\text{L})]^{1+}$  (**146**: C~N = ppy, bhq, 2-tp; L~L = dipy, phen), with various counterions, and  $\text{Ir}(\text{ppy})_3$  (**147**) were reported<sup>169-174</sup> and compared to that of  $\text{Rh}(\text{dipy})^{3+}$ .

Iridium chloride with H2-tp in refluxing 2-methoxyethanol formed a bis-cyclo-metalated dimer **148**, which was cleaved with py,  $\text{PBU}_3$ , and  $\text{Me}_2\text{SO}$  to give



monomers **149**.<sup>175</sup> Complexes **148** and **149** were characterized by IR and  $^1\text{H}$  NMR spectroscopy.



A very interesting reaction was reported,<sup>176,177</sup> in which  $[\text{Ir}(\text{cod})(\text{PPh}_3)_2][\text{SbF}_6]$  was treated with Hbhq under 1 atm of  $\text{H}_2$  and a trace of  $\text{H}_2\text{O}$  to give  $\text{Ir}(\text{bhq})(\text{PPh}_3)_2(\text{H})\text{H}_2\text{O}$  (**150**). In the presence of  $\text{H}_2$ , one molecule of  $\text{H}_2$  displaces the  $\text{H}_2\text{O}$  in **150** to give **151** in which  $\text{H}_2$  is undissociatively bound. This dihydrogen complex appeared to be in equilibrium with the trihydride **152**. Reaction of **151** with  $\text{MeLi}$  gave the dihydride **153**.

Various transition metal carbonyls were found to form both mono- and bis-



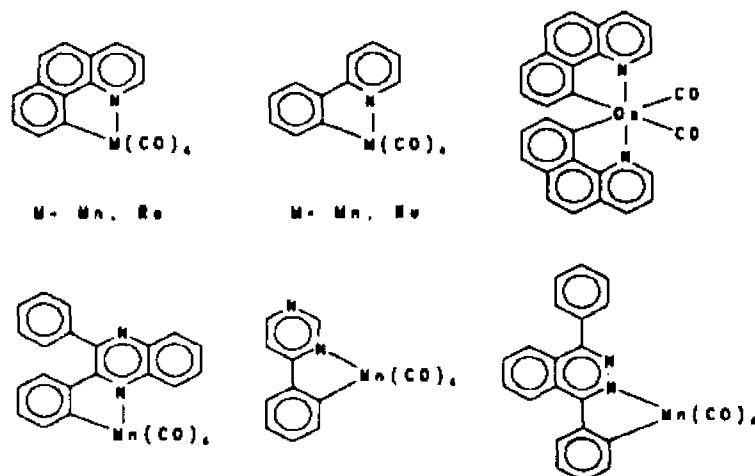
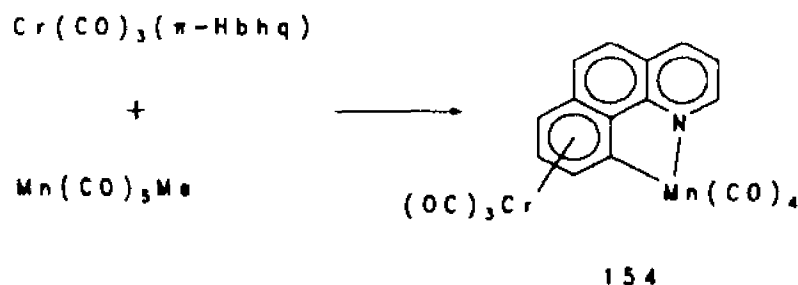


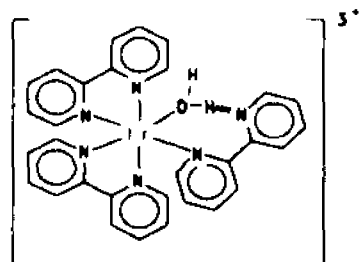
Figure 10. Cyclometalated Transition Metal Carbonyl Complexes of Pyridinyl Ligands.

cyclometalated complexes depending on the metal used.<sup>159,178</sup> Figure 10 shows the different complexes prepared. In addition, the novel hetero-dinuclear complex **154** was prepared<sup>159</sup> from  $\text{Cr}(\text{CO})_3(\pi\text{-Hbhq})$  and  $\text{Mn}(\text{CO})_5\text{Me}$ .

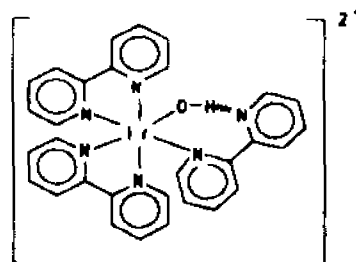


### 2,2'-Dipyridine as a *N,C*-Chelate

In 1977 Watts et al. published a report<sup>179</sup> in which  $[\text{Ir}(\text{dipy})_2(\text{H}_2\text{O})(\text{dipy})]\text{Cl}_3 \cdot \text{H}_2\text{O}$  (**155**) was proposed to possess one dipy as a monodentate ligand. This instigated a vigorous discussion in the literature concerning its structure. Two years later Watts and Bergeron published<sup>180</sup> what was claimed to be the first observation of proton phototautomerism in a transition metal complex i.e. **155**. In the same year Kahl et al. reported<sup>181</sup> the detailed NMR spectrum of **155** and its conjugate base **156**, whose

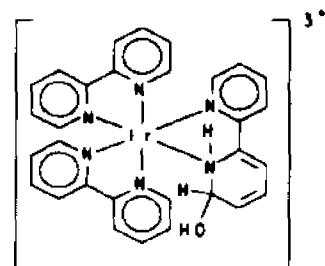


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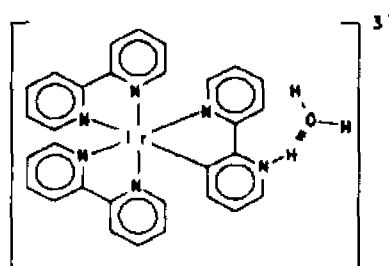


156

$^1\text{H}$  NMR spectrum showed a doublet at an abnormally low  $\delta$  value ( $\approx 6.9$  ppm). Gillard et al. reported<sup>182</sup> the  $^1\text{H}$  NMR spectrum of **155** and also found an upfield doublet at 6.77 ppm which they believed was due to a tetrahedral carbon and thus postulated **157** as the actual structure of **155**. In a rebuttal by Spellane and Watts,<sup>183</sup> the  $^{13}\text{C}$  NMR spectrum of **155** was reported which showed that no signal was present below 120 ppm that would correspond to a tetrahedral carbon and thus maintained that **155** was the actual structure.



157



158

Finally, in 1981, Wickramasinghe et al.<sup>184</sup> disproved both **155** and **157** as the correct structure by reporting the X-ray crystal structure of "[Ir(dipy)<sub>2</sub>(H<sub>2</sub>O)(dipy)]<sup>3+</sup>" which contains a *N,C*-bidentate dipy ligand (**158**). Although it was not actually determined that there was a Ir-C bond, the fact that a H<sub>2</sub>O molecule was hydrogen bonded to the pyridine ring led to that conclusion. They noted that the structure

determination did not discount the possibility of a *C,C*-chelate of dipy. The 500-MHz proton and 125-MHz  $^{13}\text{C}$  NMR spectra of **158** were reported<sup>185</sup> and completely assigned. The X-ray crystal structure of the conjugate base of **158** was reported<sup>186</sup> and it also contained a *N,C*-bidentate dipy ligand. These authors pointed out that the signal at  $\approx 6.7$  ppm in the  $^1\text{H}$  NMR spectrum, which was assigned to the 4-pyrH of the *C*-bonded pyridine ring, may be diagnostic for *N,C*-chelated octahedral dipy complexes of this type (this upfield shift is probably due to the close proximity of an orthogonal pyridine ring of one of the *N,N'*-chelated dipy ligands). If this is the case, then  $\text{Pt}(\text{dipy})(\text{CN})_2 \cdot \text{H}_2\text{O}$ , which was reported<sup>187</sup> to be a covalent hydrate (e. g. **157**) due to the  $^1\text{H}$  NMR signal at  $\approx 6.8$  ppm, may in fact be a *N,C*-chelate. Constable and Seddon also reported<sup>188</sup> H/D exchange at the 3,3'-positions of  $[\text{Ru}(\text{dipy})_3]^{2+}$  in  $\text{Me}_2\text{SO}-d_6$  with  $\text{NaOCD}_3$  in  $\text{CD}_3\text{OD}$ ; this exchange was later postulated<sup>189</sup> to proceed through an intermediate cyclometalated species.

## 2-Vinylpyridine as a *N,C*-chelate

Considering the greater reactivity of an isolated carbon-carbon double bond as compared to benzene, the cyclometalation of 2-vinylpyridine (2-vp) would be expected to be more facile than 2-phenylpyridine for example. However, to the best of our knowledge, there are very limited reports of cyclometalated 2-vp (or its derivatives) complexes. The rationale for this is probably due to the accepted mechanism of the reaction. The first step is the straightforward formation of the M-N bond. Next, electrophilic attack of the metal on the double bond (2-vp) or aromatic ring (2-arylpyridine) occurs generating a positive charge on the carbon alpha to the pyridine. In 2-arylpyridines, this positive charge is stabilized by delocalization in the carbocyclic ring, but in 2-vp, delocalization would result in disruption of the

aromaticity of the pyridine ring. The charge thus resides mostly on the alpha carbon, which is a secondary carbocation possessing an electron-withdrawing group (pyridine)

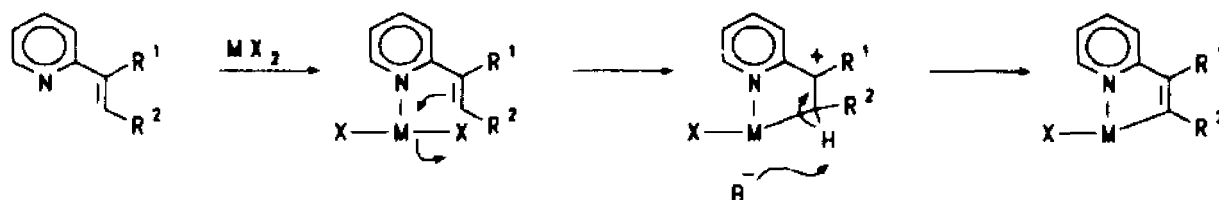
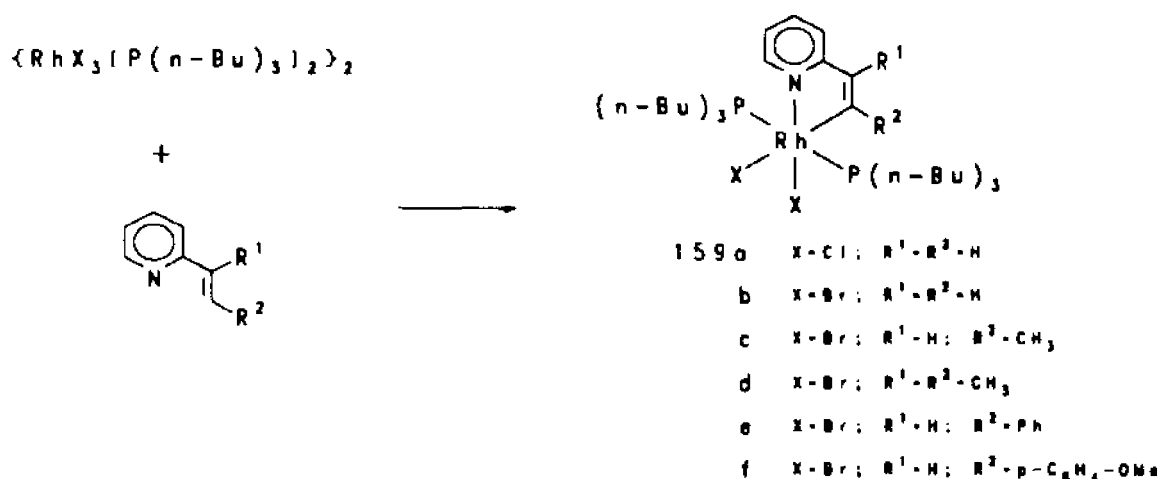


Figure 11. Mechanism for Cyclometalation of 2-Vinylpyridine with  $MX_2$ .

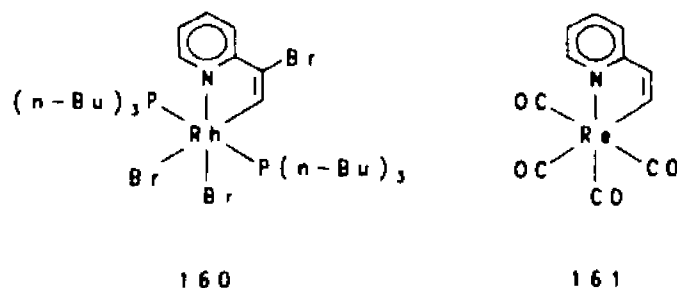
destabilizing the cation even further. To circumvent this, a very electrophilic metal must be used or the cation intermediate must be stabilized by suitable electron-donating substituents ( $R^1$ ). The final step in the mechanism is deprotonation at the beta position to regenerate a double bond.

In 1973, the first cyclometalated 2-vp complex was reported<sup>190</sup> in which  $[RhX_3(P(n-Bu)_3)_2]_2$  was reacted with 2-vp to give **159a,b**. In the full account,<sup>191</sup> several other complexes of 2-vp derivatives **159c-f** were reported. In the  $^1H$  NMR spectra of **159**, the  $\beta$ -alkenyl protons ( $R^2$ ) were shifted downfield to 9.30-9.38 ppm and in the  $^{13}C$

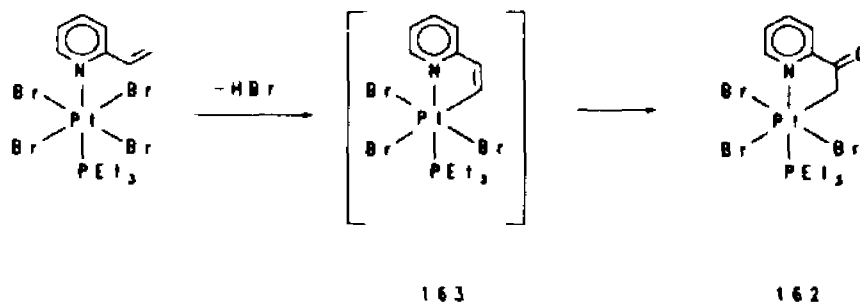


NMR spectra, the  $\beta$ -alkenyl carbons were shifted extremely downfield and ranged from 186.0 to 196.9 ppm. Complexes **159b** and **159c** underwent an interesting addition reaction with  $\text{Br}_2$  followed by elimination of  $\text{HBr}$  to give **160**; whereas **159** did not react with nucleophiles,  $\text{CO}$ , or equimolar  $\text{HBr}$ , although excess  $\text{HBr}$  displaced the 2-(alkenyl)pyridine.

Bruce et al. reported<sup>178</sup> the synthesis of **161** which was structurally supported by analytical and IR data. The mass spectrum of **161** contained ions up to  $m/e$  744 which was attributed to thermal decomposition; without further evidence the actual structure of **161** is yet uncertain.



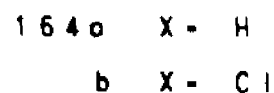
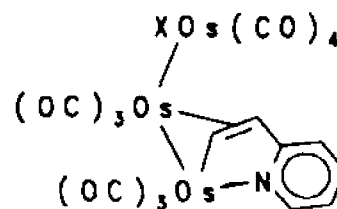
When  $\text{PtBr}_4(2\text{-vp})(\text{PEt}_3)$  was recrystallized from wet solvents, **162** was formed; the proposed intermediate **163** (which was not isolable) was transformed to **162** by



reaction with water and subsequent oxidation.

2-Vinylpyridine reacted with  $[\text{Os}_3\text{H}_2(\text{CO})_{10}]$  to give the triosmium cluster  $[\text{Os}_3\text{H}(\text{CO})_{10}(2\text{vp})]$  (**164a**)<sup>192</sup> which contained a cyclometalated 2-vp ligand. The

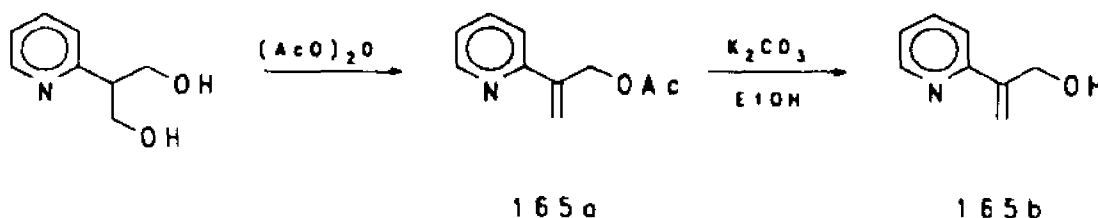
ethenyl moiety was also intramolecularly bonded to another osmium center via a  $\pi$ -bond which was proven by an X-ray crystal structure determination; reaction of **164a** with  $\text{CCl}_4$  gave the chloro derivative **164b**. Although structurally different than **159** and **160**, clusters **164** showed similar  $^1\text{H}$  NMR resonances at  $\approx 9.20$  attributed to the  $\beta$ -alkenyl protons. Other related complexes were also reported.<sup>192</sup>



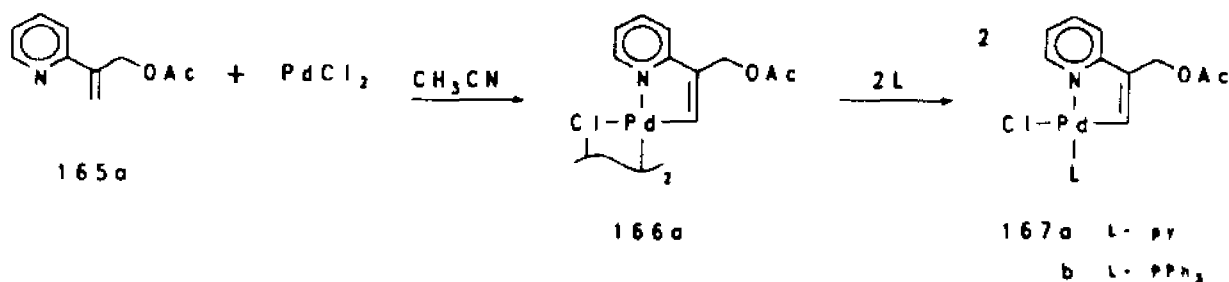
## Results

### Syntheses

Dichloropalladium(II) does not readily undergo cyclometalation with 2-vp because of the formation of an intermediate secondary carbocation (see Figure 11). To circumvent this problem, the  $\alpha$ -substituted derivative **165** was chosen for cyclometalation for two reasons: 1)  $\alpha$ -substitution would generate a more stable tertiary cation in the intermediate, and 2) a functionalized  $\alpha$ -substituent would allow such uses as polymer functionalization, synthesis of dinuclear complexes, easy ligand modification, etc.



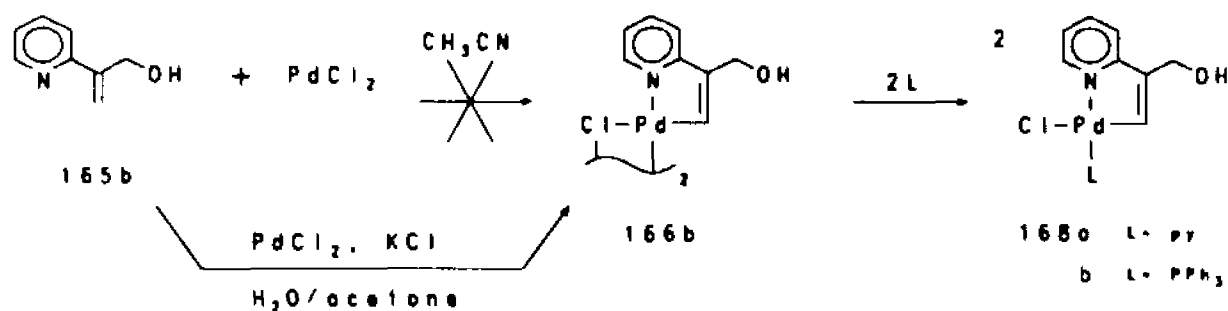
Ligand **165a** was easily synthesized by the method of Bohlmann, et al.<sup>193</sup> from the commercially available<sup>194</sup> 2-(2-pyridinyl)-1,3-propanediol. Treatment of the propanediol with acetic anhydride at reflux for 6h yielded (94%) **165a** which underwent facile transesterification with anhydrous  $\text{K}_2\text{CO}_3$  in absolute EtOH to give (57%) **165b**.



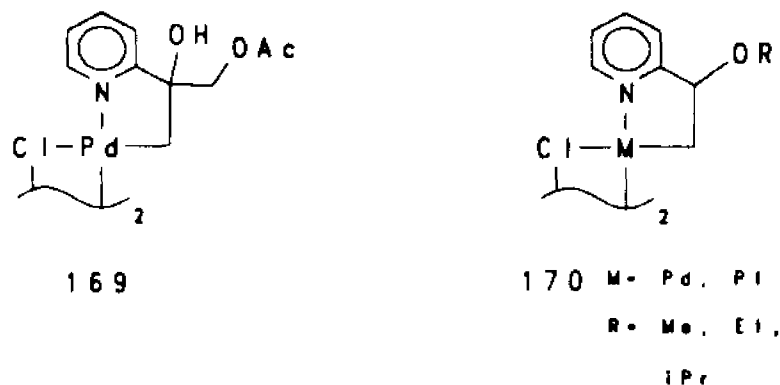
Cyclometalation of **165a** with  $\text{PdCl}_2$  occurred at 25 °C in  $\text{CH}_3\text{CN}$  to give (47%) the chloro-bridged dimer **166a**; addition of  $\text{K}_2\text{CO}_3$  increased the yield to 67%. The

2:1-complex  $\text{PdCl}_2(\mathbf{165a})_2$  could not be obtained under these conditions using two equivalents of ligand. Dimer **166a** reacted, as expected, with either pyridine or  $\text{P(Ph)}_3$  to give monomers **167**.

Although reaction of **165b** with  $\text{PdCl}_2$  in  $\text{CH}_3\text{CN}$  *did not* give  $[\text{PdCl}(\mathbf{165b})]_2$  (**166b**), the use of  $\text{K}_2\text{PdCl}_4$  (generated in situ) in  $\text{H}_2\text{O}/\text{acetone}$  did yield (96%) dimer **166b**, which also reacted with either pyridine or  $\text{P(Ph)}_3$  to give monomers **168**.



Because of the high yield (96%) of **166b** when the reaction was conducted in  $\text{H}_2\text{O}/\text{acetone}$ , these conditions were tried on ligand **165a** to give (74%) dimer **166a**. When excess **165a** was used, the yield was generally lower (50–60%). Dimer **169** was sometimes isolated under these conditions in varying (10–40%) yields. A similar product was reported<sup>195</sup> when 2-vp was reacted with  $\text{Na}_2\text{MCl}_4$  (M = Pd, Pt) in various alcohols to give complexes **170**.





Foot and Heaton reported<sup>190,191</sup> the synthesis of complex **171** by reaction of the 2-vp complex with Br<sub>2</sub>. When dimer **166a** was reacted with Br<sub>2</sub>, an inseparable mixture of oxidation products was obtained.

### Proton NMR Spectroscopy

A comparison of the chemical shifts of the 6-pyridinyl protons shows a gradual *downfield* shift when the ligands ( $\approx 8.5$  ppm) are compared to the dimers ( $\approx 8.8$  ppm) which are in turn compared to the monomers (9.03 - 9.36 ppm). These shifts are probably due to the difference in the electron-withdrawing effects of the metal centers on the pyridine rings as well as the trans effects in the complexes.

The most important shifts in the <sup>1</sup>H NMR spectra are those of the vinyl protons. For the allyl acetate and alcohol ligands these resonances appear at 5.56/5.99 ppm and 5.50/5.78 ppm, respectively. The analogous cyclometalated complexes show the disappearance of one resonance and the collapse to a singlet of the other resonance which is shifted *downfield* relative to the analogous ligand. The allyl acetate complexes range from 6.63 - 7.04 ppm and the allyl alcohol complexes range from 6.20 - 6.80 ppm. These shifts are in the same range as those observed by Foot and Heaton<sup>190,191</sup> for complexes **159** and again are due to an electron-withdrawing effect of the metal on the vinyl carbons. The only other shifts are a slight *upfield* shift ( $\approx 0.4$  ppm) of the allyl-CH<sub>2</sub> protons observed on complexation.

### Carbon-13 NMR Spectroscopy

The only extreme shifts in the <sup>13</sup>C NMR spectra are those of the  $\beta$ -alkenyl carbons which exhibit large downfield shifts upon complexation from  $\approx 116$  ppm in the ligands to  $\approx 168$  ppm in the complexes; similar shifts are observed in the related complexes **159**<sup>190,191</sup>. All other shifts are similar to those observed in the ligands.

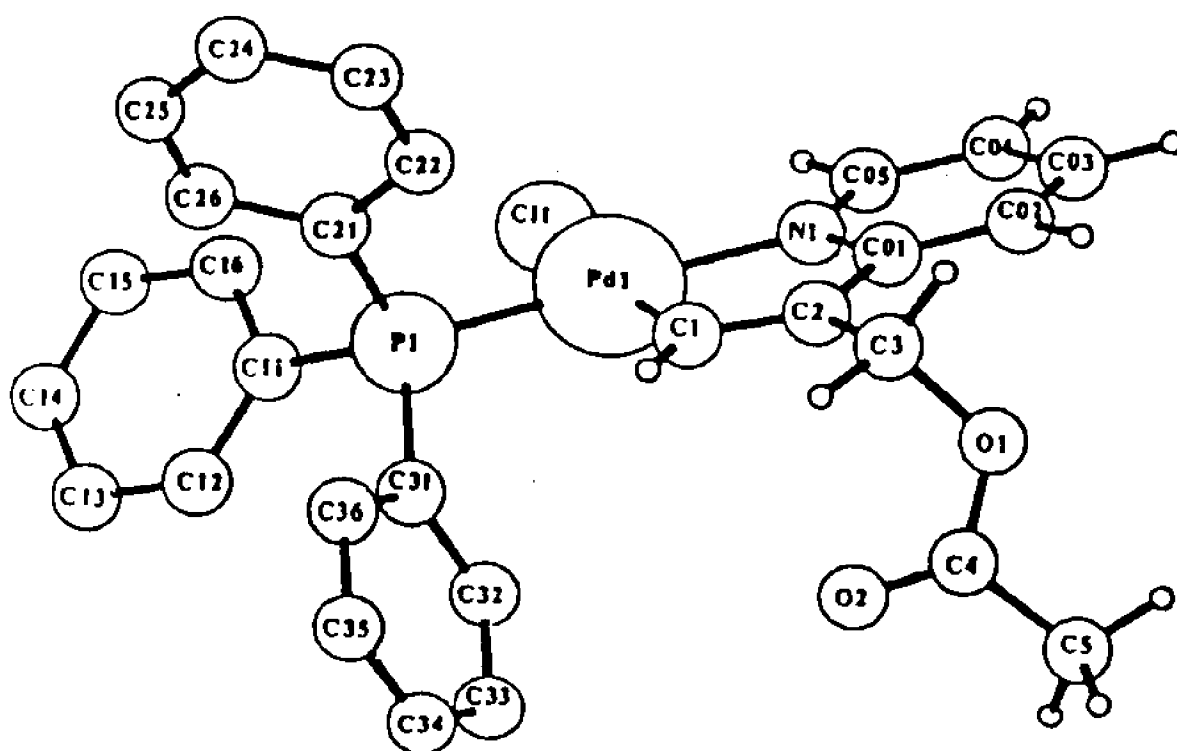


Figure 12. ORTEP drawing of  $C_{28}H_{25}NClO_2PPd$ .

## Structure Determination

An X-ray crystal structure determination of **167b** has been done<sup>196</sup> to verify the existence of the carbon-metal bond [1.982(5) Å]; an ORTEP drawing is shown in Figure 12. The carbon-carbon double bond is also intact [1.328(8) Å].

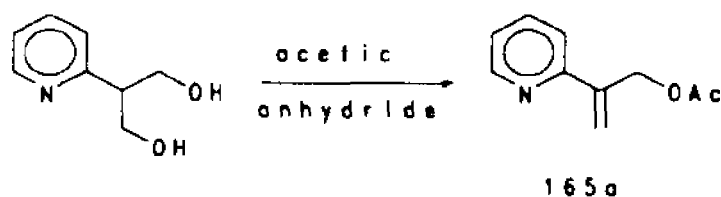
## Conclusion

Novel dimeric cyclometalated complexes of 2-vinylpyridine derivatives and their pyridine and PPh<sub>3</sub> monomers that possess Pd-C<sub>sp<sup>2</sup></sub> sigma bonds, in which the sp<sup>2</sup> carbon is part of a vinyl (allyl) system rather than in an aromatic ring, have been synthesized and characterized by <sup>1</sup>H NMR and <sup>13</sup>C NMR spectroscopy. An X-ray crystal structure determination of one of the monomers proved the existence of the Pd-C sigma bond.

## Experimental

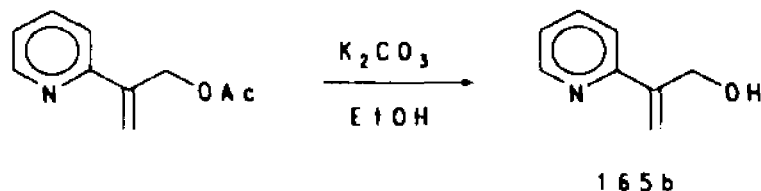
**General Comments.** are found on page 65 in Chapter 1.

**Reagents.** Unless otherwise noted, all reagents and solvents utilized were of reagent grade and no further purification was undertaken. 2-(2-Pyridinyl)-1,3-propanediol was purchased from Aldrich Chemical Co., Milwaukee, Wisconsin<sup>194</sup>.

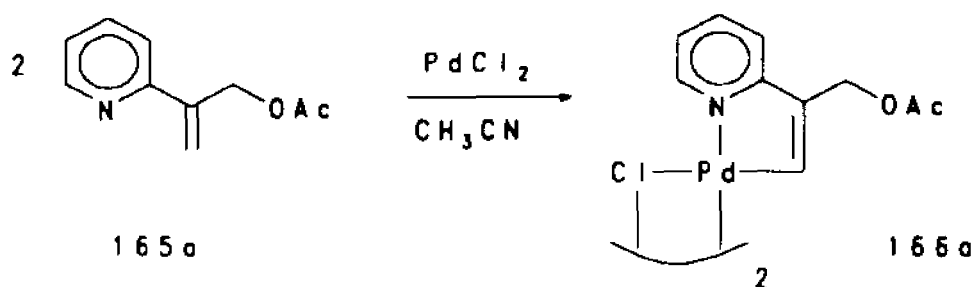


**2-(2-Pyridinyl)-3-acetoxyprene (165a).** A stirred solution of 2-(2-pyridinyl)-1,3-propanediol<sup>193</sup> (10.36 g, 6.77 mmol) in Ac<sub>2</sub>O (75 mL) was refluxed for 6h. The

Ac<sub>2</sub>O was removed in vacuo to give a thin oil, which was distilled under reduced pressure to give (94%) **165a**,<sup>193,197</sup> as a colorless liquid: 11.27g; bp 105-115 °C(1 mm) [lit<sup>193</sup> bp 120-130 °C(3mm)]; <sup>1</sup>H NMR δ 2.09 (s, CH<sub>3</sub>, 3H), 5.16 (d, CH<sub>2</sub>, *J* = 1.4 Hz, 1H), 5.56 (dd, CH<sub>cis pyr</sub>, <sup>2</sup>*J* = 0.9, <sup>4</sup>*J* = 1.4 Hz, 1H), 5.99 (d, CH<sub>trans pyr</sub>, <sup>2</sup>*J* = 0.9 Hz, 1H), 7.18 (ddd, 5-pyrH, *J*<sub>4,5</sub> = 7.0, *J*<sub>5,6</sub> = 4.8, *J*<sub>3,5</sub> = 1.7 Hz, 1H), 7.42-7.55 (m, 3-pyrH, 1H), 7.58-7.79 (m, 4-pyrH, 1H), 8.58 (ddd, 6-pyrH, *J*<sub>5,6</sub> = 4.8, *J*<sub>4,6</sub> = 1.7, *J*<sub>3,6</sub> = 1.0 Hz, 1H); <sup>13</sup>C NMR δ 20.8 (CH<sub>3</sub>), 64.6 (CH<sub>2</sub>), 117.1 (=CH<sub>2</sub>), 120.2 (C3), 122.7 (C5), 136.5 (C4), 142.6 (=CR<sub>2</sub>), 149.2 (C6), 156.0 (C2), 170.9 (CO); MS *m/z* 177(2), 134(100), 78(15), 43(19).



**2-(2-Pyridinyl)-3-hydroxypropene (165b).** A stirred solution of 2-(2-pyridinyl)-3-acetoxypropene (490 mg, 2.77 mmol) and anhydrous K<sub>2</sub>CO<sub>3</sub> (300 mg, 2.16 mmol) in EtOH (50 mL) was refluxed for 15 h. After concentration, the resulting solid was extracted with CH<sub>2</sub>Cl<sub>2</sub>, the solvent removed in vacuo and the resulting oil distilled under reduced pressure to give (71%) pure **165b**<sup>197</sup>: 213 mg; bp 135-145 °C(1 mm); <sup>1</sup>H NMR δ 4.60 (s, CH<sub>2</sub>, 1H), 5.50 (s, CH<sub>cis pyr</sub>, 1H), 5.78 (s, CH<sub>trans pyr</sub>, 1H), 7.18 (ddd, 5-pyrH, *J*<sub>4,5</sub> = 6.8, *J*<sub>5,6</sub> = 4.8, *J*<sub>3,5</sub> = 2.0 Hz, 1H), 7.55-7.82 (m, 3-pyrH, 1H), 7.63-7.77 (m, 4-pyrH, 1H), 8.50 (ddd, 6-pyrH, *J*<sub>5,6</sub> = 4.8, *J*<sub>4,6</sub> = *J*<sub>3,6</sub> = 1.2 Hz, 1H); <sup>13</sup>C NMR δ 65.6 (CH<sub>2</sub>), 115.8 (=CH<sub>2</sub>), 120.1 (C3), 122.4 (C5), 136.6 (C4), 145.9 (=CR<sub>2</sub>), 148.3 (C6), 157.4 (C2); MS *m/z* 135(22), 134(36), 117(5), 106(100), 105(19), 104(37), 79(28), 78(62).

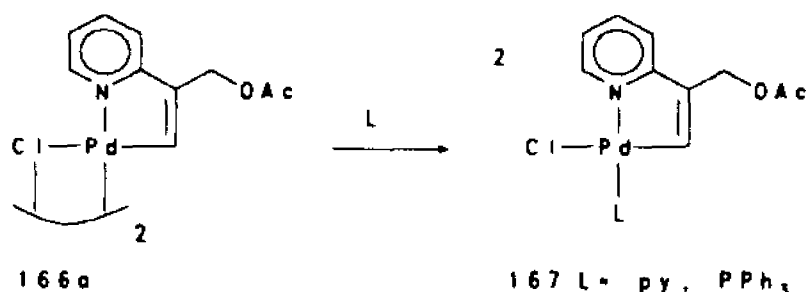


**$\mu$ -Dichloro-bis[2-(2-pyridinyl)-3-acetoxypentenyl-*C,N*]dipalladium(II) (166a).**

**Method A:** A solution of  $\text{PdCl}_2$  (297 mg, 1.67 mmol), allyl acetate **165a** (302 mg, 1.71 mmol), and anhydrous  $\text{K}_2\text{CO}_3$  (470 mg, 3.40 mmol) in  $\text{CH}_3\text{CN}$  (100 mL) was stirred for 12h at 25 °C. The solvent was then removed in vacuo and the resulting solid triturated with  $\text{CHCl}_3$ . After removing the  $\text{CHCl}_3$ , the mixture was purified using dry-flash chromatography ( $\text{SiO}_2$ ) eluting with  $\text{CHCl}_3$  to give (67%) **166a**, as light yellow microcrystals: 362 mg; mp >255 °C (dec);  $^1\text{H}$  NMR ( $\text{Me}_2\text{SO}-d_6$ )  $\delta$  2.01 (s,  $\text{CH}_3$ , 3H), 4.76 (s,  $\text{CH}_2$ , 2H), 7.04 (s,  $\text{CH}$ , 1H), 7.34 (dd, 3-pyrH,  $J_{3,4} = 7.8$ ,  $J_{3,5} = 1.4$  Hz, 1H), 7.37 (ddd, 5-pyrH,  $J_{5,6} = 4.7$ ,  $J_{4,5} = 7.7$ ,  $J_{3,5} = 1.4$  Hz, 1H), 8.03 (ddd, 4-pyrH,  $J_{4,5} = J_{3,4} = 7.7$ ,  $J_{4,6} = 1.7$  Hz, 1H), 8.85 (bd, 6-pyrH,  $J_{5,6} = 4.7$  Hz, 1H);  $^{13}\text{C}$  NMR ( $\text{Me}_2\text{SO}-d_6$ )  $\delta$  20.4 ( $\text{CH}_3$ ), 62.1 ( $\text{CH}_2$ ), 119.9 (C3), 122.2 (C5), 140.9 (C4), 142.3 ( $=\text{CR}_2$ ), 150.0 (C6), 165.2 (C2), 170.1 (CO), 171.6 (PdC); IR (KBr) 1732s ( $\text{C}=\text{O}$ ), 1603, 1480s ( $\text{C}=\text{C}$ ,  $\text{C}=\text{N}$ ), 1264s, 1030 ( $\text{C}-\text{O}$ ), 826, 776  $\text{cm}^{-1}$ ; Anal. Calcd for  $\text{C}_{20}\text{H}_{20}\text{N}_2\text{Cl}_2\text{O}_4\text{Pd}_2$ : C, 37.76; H, 3.17; N, 4.40; Cl, 11.15. Found C, 37.73; H, 3.18; N, 4.32; Cl, 10.91.

**Method B.** A solution of allyl acetate **165a** (131 mg, 740  $\mu\text{mol}$ ) in acetone (15 mL) was added to a stirred solution of  $\text{PdCl}_2$  (132 mg, 744  $\mu\text{mol}$ ) and KCl (165 mg, 2.21 mmol) in  $\text{H}_2\text{O}$  (10 mL) and the solution was stirred at 25 °C for 12 h. The mixture was then filtered to give (74%) **166a**, as a light yellow solid (176 mg).

In some reactions, a by-product was also isolated and shown to be dimer **169** (10-40%): mp >280 °C;  $^1\text{H}$  NMR ( $\text{Me}_2\text{SO}-d_6$ )  $\delta$  2.00 (s,  $\text{CH}_3$ , 3H), 2.18 (d,  $\text{PdCH}_2$ ,  $^2J = 9.2$  Hz, 1H), 2.62 (d,  $\text{PdCH}_2$ ,  $^2J = 9.2$  Hz, 1H), 4.21 (d,  $\text{OCH}_2$ ,  $^2J = 11.1$  Hz, 1H), 4.38 (d,  $\text{OCH}_2$ ,  $J_{\text{gem}} = 11.1$  Hz, 1H), 6.07 (s, OH, 1H), 7.47-7.59 (m, 3,5-pyrH, 2H), 8.07 (ddd, 4-pyrH,  $J_{3,4} = J_{4,5} = 7.3$ ,  $J_{4,6} = 1.4$  Hz, 1H), 8.89 (d, 6-pyrH,  $J_{5,6} = 5.5$  Hz, 1H);  $^{13}\text{C}$  NMR ( $\text{Me}_2\text{SO}-d_6$ )  $\delta$  20.1 ( $\text{CH}_3$ ), 39.1 ( $\text{PdCH}_2$ ), 70.4 ( $\text{CH}_2\text{O}$ ), 80.7 ( $\alpha\text{C}$ ), 123.3, 123.6 (C3 & C5), 138.9 (C4), 148.5 (C6), 168.9, 169.1 (C2 & CO); IR (KBr) 3468b (OH), 1738s (C=O), 1607, 1478 (C=C, C=N), 1250, 1048 (C-O)  $\text{cm}^{-1}$ ; Anal. Calcd for  $\text{C}_{20}\text{H}_{24}\text{N}_2\text{Cl}_2\text{O}_6\text{Pd}_2$ : C, 35.74; H, 3.60; N, 4.17. Found: C, 35.89; H, 3.63; N, 4.16.

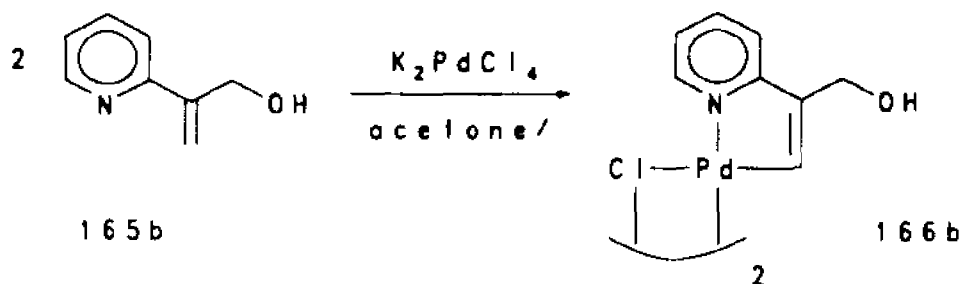


**Chloro[2-(2-pyridinyl)-3-acetoxypentenyl-*C,N*]pyridinepalladium(II) (**167a**).**

Excess pyridine ( $\approx 600$  mg) was added to a stirred solution of **166a** (63 mg, 0.1 mmol) in  $\text{CH}_2\text{Cl}_2$  (10 mL) and after stirring for 12h at 25 °C the solvent was removed. Purification by column chromatography ( $\text{SiO}_2$ ) eluting with  $\text{CH}_2\text{Cl}_2$  gave (100%) **167a**, as a yellow solid: 80 mg; mp 189-190 °C (dec);  $^1\text{H}$  NMR  $\delta$  2.06 (s,  $\text{CH}_3$ , 3H), 4.79 (s,  $\text{CH}_2$ , 2H), 6.99 (s,  $=\text{CH}$ , 1H), 7.05-7.15 (m, 3,5-pyrH, 2H), 7.44 (dd, 3'-pyrH,  $J_{3,4} = 7.1$ ,  $J_{2,3} = 7.1$  Hz, 2H), 7.70-7.95 (m, 4-, 4'-pyrH, 2H), 8.85 (d, 2'-pyrH,  $J_{2,3} = 7.1$  Hz, 1H), 9.25 (d, 6-pyrH,  $J_{5,6} = 4.7$  Hz, 1H);  $^{13}\text{C}$  NMR  $\delta$  20.7 ( $\text{CH}_3$ ), 62.5 ( $\text{CH}_2$ ), 118.8 (C3), 121.0 (C5), 125.2 (C3'), 138.0, 138.9 (C4 & C4'), 142.2 ( $=\text{CR}_2$ ), 152.1 (C6), 153.1 (C2'), 166.2, 166.9 (C2 & Pd-C), 170.3 (CO); IR

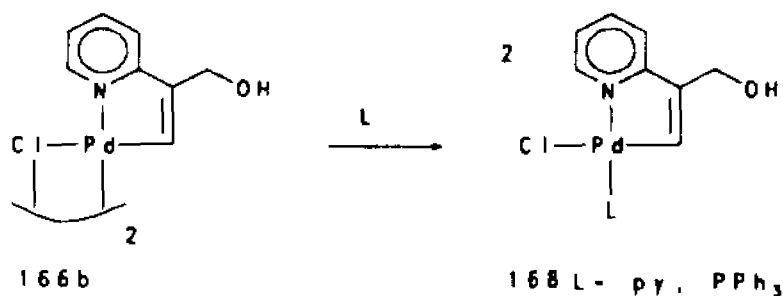
(KBr) 1721 (C=O), 1447, 1480 (C=C, C=N), 1223, 1028 (C-O), 830, 760, 696  $\text{cm}^{-1}$ ; Anal. Calcd for  $\text{C}_{15}\text{H}_{15}\text{N}_2\text{ClO}_2\text{Pd}$ : C, 45.36; H, 3.81; N, 7.05. Found: C, 45.22; H, 3.86; N, 7.00.

**Chloro[2-(2-pyridinyl)-3-acetoxypentenyl-*C,N*]triphenylphosphinepalladium(II) (167b).** A solution of **166a** (71 mg, 0.11 mmol) and triphenylphosphine (64 mg, 0.24 mmol) in  $\text{CH}_2\text{Cl}_2$  (20 mL) was stirred for 18h at 25 °C. The solvent was then removed to give (95%) **167b**, as a yellow solid: 123 mg; mp 187-188 °C (dec).  $^1\text{H}$  NMR  $\delta$  1.98 (s,  $\text{CH}_3$ , 3H), 4.61 (s,  $\text{CH}_2$ , 2H), 6.63 (d,  $=\text{CH}$ ,  $J_{\text{P,H}} = 19.0$  Hz, 1H), 7.10 (d, 3-pyrH,  $J_{3,4} = 7.9$  Hz, 1H), 7.19 (dd, 5-pyrH,  $J_{4,5} = 7.5$ ,  $J_{5,6} = 4.4$  Hz, 1H), 7.39-7.49 (m, 2,4,6-phH, 9H), 7.60-7.78 (m, 3,5-phH & 4-pyrH, 7H), 9.36 (t, 6-pyrH,  $J_{5,6} = J_{\text{P,H}} = 4.4$  Hz, 1H);  $^{13}\text{C}$  NMR (400 MHz)  $\delta$  20.9 ( $\text{CH}_3$ ), 64.2 ( $\text{CH}_2$ ), 118.5 (C3), 121.4 (C5,  $J_{\text{P,C}} = 3$  Hz), 128.4 (C3',  $J_{\text{P,C}} = 11.1$  Hz), 130.2 (C1',  $J_{\text{P,C}} = 52.3$  Hz), 130.8 (C4',  $J_{\text{P,C}} = 2.0$  Hz), 134.7 (C2',  $J_{\text{P,C}} = 12.1$  Hz), 139.2 (C4), 142.6 ( $=\text{CR}_2$ ), 150.0 (C6), 164.3 (C2,  $J_{\text{P,C}} = 4.0$  Hz), 170.1 (Pd-C,  $J_{\text{P,C}} = 4.0$  Hz), 170.6 (CO); IR (KBr) 1742s (C=O), 1603, 1480 (C=C, C=N), 1435s (P-C), 1219s, 1096 (C-O), 750, 694  $\text{cm}^{-1}$ ; Anal. Calcd for  $\text{C}_{28}\text{H}_{25}\text{NClO}_2\text{PPd}$ : C, 57.95; H, 4.34; N, 2.41. Found: C, 57.80; H, 4.52; N, 2.16.



**$\mu$ -Dichloro-bis[2-(2-pyridinyl)-3-hydroxypropenyl-*C,N*]dipalladium(II) (166b).** Allyl alcohol **165b** (300 mg, 2.22 mmol) in acetone (5 mL) was added to a stirred solution of  $\text{PdCl}_2$  (200 mg, 1.13 mmol) and KCl (300 mg, 4.02 mmol) in  $\text{H}_2\text{O}$  (15

mL). After stirring for 16h at 27 °C, the mixture was filtered and washed with acetone to give (96%) **166b**·H<sub>2</sub>O, as a yellow solid: 310 mg; mp 217 °C (dec); <sup>1</sup>H NMR (Me<sub>2</sub>SO-*d*<sub>6</sub>) δ 4.16 (s, CH<sub>2</sub>, 2H), 6.80 (s, =CH, 1H), 7.27-7.55 (m, 3,5-pyrH, 2H), 8.00 (ddd, 4-pyrH,  $J_{3,4} = J_{4,5} = 7.8$ ,  $J_{4,6} = 1.7$  Hz, 1H), 8.83 (d, 6-pyrH,  $J_{5,6} = 4.5$  Hz, 1H); <sup>13</sup>C NMR (Me<sub>2</sub>SO-*d*<sub>6</sub>) δ 60.4 (CH<sub>2</sub>), 120.4 (C3), 121.9 (C5), 140.6 (C4), 148.1 (C6), 149.9 (αC), 166.3 (PdC), 166.4 (C2); IR (KBr) 3337b (OH), 1599s, 1482s (C=C, C=N), 1080 (C-O), 822, 762 cm<sup>-1</sup>; Anal. Calcd for C<sub>16</sub>H<sub>16</sub>N<sub>2</sub>Cl<sub>2</sub>O<sub>2</sub>Pd<sub>2</sub>·H<sub>2</sub>O: C, 33.71; H, 3.18; N, 4.91. Found: C, 33.81; H, 3.42; N, 4.78.



**Chloro[2-(2-pyridinyl)-3-hydroxypropenyl-*C,N*]pyridinepalladium(II) (168a).**

An excess of pyridine was added to a stirred suspension of **166b** (85 mg, 0.15 mmol) in CHCl<sub>3</sub> (25 mL). After stirring for 12h at 25 °C the solvent was removed and the resulting solid was purified on a SiO<sub>2</sub> column eluting with CHCl<sub>3</sub> to give (66%) **168a**, as a yellow solid: 72 mg; mp 138-141 °C; <sup>1</sup>H NMR δ 1.56 (t, OH,  $J = 5.8$  Hz, 1H), 4.36 (d, CH<sub>2</sub>,  $J = 5.8$  Hz, 2H), 6.83 (s, =CH, 1H), 7.07 (ddd, 5-pyrH,  $J_{4,5} = 7.3$ ,  $J_{5,6} = 5.6$ ,  $J_{3,5} = 1.4$  Hz, 1H), 7.18-7.85 (m, 3,3'-pyrH, 3H), 7.88-7.96 (m, 4,4'-pyrH, 2H), 8.88 (d, 2'-pyrH,  $J_{2,3} = 5.6$  Hz, 2H), 9.25 (d, 6-pyrH,  $J_{5,6} = 5.1$  Hz, 1H); <sup>13</sup>C NMR δ 61.4 (CH<sub>2</sub>), 119.4 (C3), 120.6 (C5), 125.1 (C3'), 138.0, 138.7 (C4 & C4'), 147.0 (αC), 151.4 (C6), 152.9 (C2'), 162.0 (C2), 166.2 (PdC); IR (KBr) 3376b (OH), 1601s, 1480s, 1449s (C=C, C=N), 1084 (C-O), 820, 758, 698 cm<sup>-1</sup>; Anal. Calcd for C<sub>13</sub>H<sub>13</sub>N<sub>2</sub>ClOPd: C, 43.97; H, 3.69; N, 7.89. Found: C, 43.90; H, 3.76; N, 7.84.



**Chloro[2-(2-pyridinyl)-3-hydroxypropenyl-*C,N*]triphenylphosphinepalladium(II)** (**168b**). Triphenylphosphine (83 mg, 0.317 mmol) was added to a stirred solution of **166b** (87 mg, 0.16 mmol) in  $\text{CHCl}_3$  (10 mL). After stirring for 12h at 25 °C, the solvent was removed to give (90%) **168b**, as a yellow solid: 153 mg; mp 109-112 °C;  $^1\text{H}$  NMR  $\delta$  1.22 (t, OH,  $J = 5.7$  Hz, 1H), 4.17 (d,  $\text{CH}_2$ ,  $J = 5.7$  Hz, 2H), 6.20 (d,  $=\text{CH}$ ,  $J_{\text{P,H}} = 19.2$  Hz, 1H), 7.11-7.41 (m, 2,4,6-phH & 3,5-pyrH, 11H), 7.56-7.87 (m, 3,5-phH & 4-pyrH, 7H), 9.35 (dd, 6-pyrH,  $J_{5,6} = J_{\text{P,H}} = 4.4$  Hz, 1H);  $^{13}\text{C}$  NMR  $\delta$  63.1 ( $\text{CH}_2$ ), 119.4 (C3), 121.1 (C5), 128.2 (C3',  $J_{\text{P,C}} = 10.8$  Hz), 130.3 (C1',  $J_{\text{P,C}} = 50.1$  Hz), 130.6 (C4'), 134.5 (C2',  $J_{\text{P,C}} = 11.8$  Hz), 139.1 (C4), 148.1 ( $\alpha\text{C}$ ), 149.5 (C6), 164.7 (C2), 165.6 (PdC); IR (KBr) 3422b (OH), 1601, 1480 (C=C, C=N), 1435s (P-C), 1098 (C-O), 746, 694s  $\text{cm}^{-1}$ ; Anal. Calcd for  $\text{C}_{26}\text{H}_{23}\text{NClOPPd}$ : C, 58.01; H, 4.31; N, 2.60 Found: C, 58.06; H, 4.57; N, 2.55.

## Chapter 3. Methyl Functionalization of 2-Methyl- and 2,7-Dimethyl-1,8-Naphthyridine

### Introduction

In 1967, Paudler and Kress first reported a feasible one-step synthesis of 2,7-dimethyl-1,8-naphthyridine [dmnap(s)],<sup>198</sup> 2-methyl-1,8-naphthyridine [mnap(s)],<sup>198</sup> and 1,8-naphthyridine [nap(s)]<sup>198,199</sup> from commercially available starting materials. Since then, a plethora of novel inorganic complexes have been reported using these potential bidentate ligands, ranging from dodecahedral transition metal complexes to dinuclear complexes containing bridging naps to icosahedral, twelve-coordinate lanthanide complexes. 1,8-Naphthyridine complexes have been reported for alkaline earth metals,<sup>200</sup> Cr(0),<sup>201</sup> Cr(VI),<sup>202</sup> Mo(0),<sup>201, 203</sup> W(0),<sup>201, 203b</sup> Mn(I),<sup>204</sup> Re(I),<sup>204g</sup> Fe(II),<sup>204c,e, 205</sup> Ru(0),<sup>206</sup> Ru(II),<sup>207</sup> Co(II),<sup>204c-f, 205i, 208</sup> Rh(I),<sup>209</sup> Rh(II),<sup>210</sup> Ir(I),<sup>209</sup> Ni(1.5),<sup>211</sup> (formal oxidation state) Ni(II),<sup>204b-f, 205i, 208</sup> Pd(II),<sup>212</sup> Pt(II),<sup>204b, 213</sup> Cu(I),<sup>214</sup> Cu(1.5),<sup>215</sup> (formal oxidation state) Cu(II),<sup>204b-e, 205i, 216</sup> Au(III),<sup>217</sup> Zn(II),<sup>204b-f, 205i</sup>

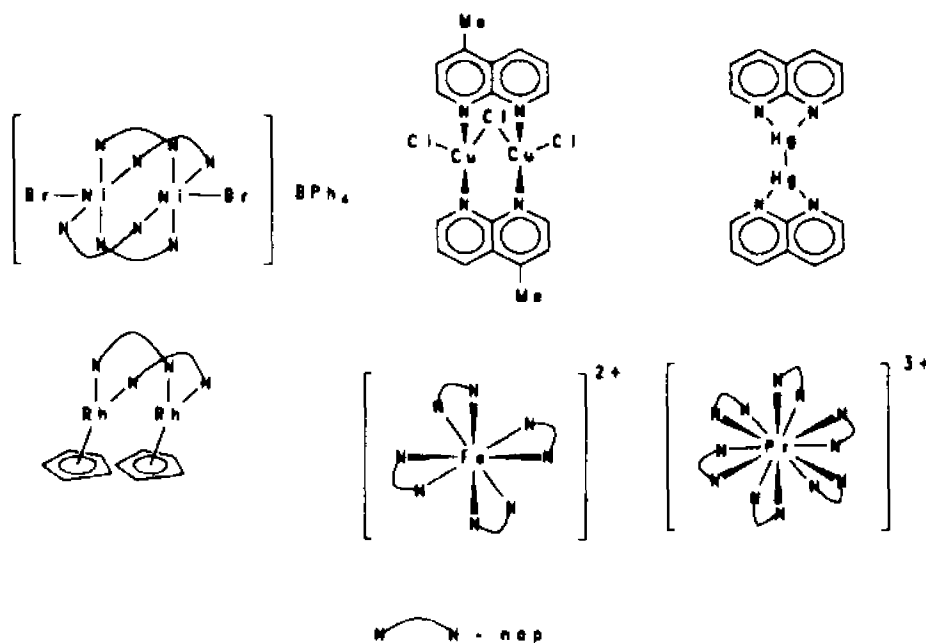


Figure 13. Interesting Examples of 1,8-Naphthyridine Complexes.

Cd(II),<sup>204b,d,e, 205i, 218</sup> Hg(I),<sup>218, 219</sup> Sn(IV),<sup>220</sup> U(III),<sup>221</sup> lanthanide metals,<sup>222</sup> and Th(IV)<sup>223</sup>. Despite this profusion of reports, very little has been done on the functionalization of these ligands in order to exploit 1,8-naphthyridines' unique complexation properties. Because of the decreased complexing ability of macrocyclic naphthyridine ligands possessing heteroatoms at the two position<sup>224, 225</sup> it was of interest to devise a method for the  $\alpha$ -carbon functionalization of 2-methyl- and 2,7-dimethyl-1,8-naphthyridines.

Since Paudler and Kress' first report<sup>198</sup> on the synthesis of 1,8-naphthyridines, other modifications have been described<sup>226</sup> making these ligands readily available. Although most syntheses of dmnap have focused on the Skraup synthesis in which 2-amino-6-picoline is combined with crotonaldehyde, this procedure is difficult due to the extreme ease and exothermicity of polymerization of crotonaldehyde. Alternatively,

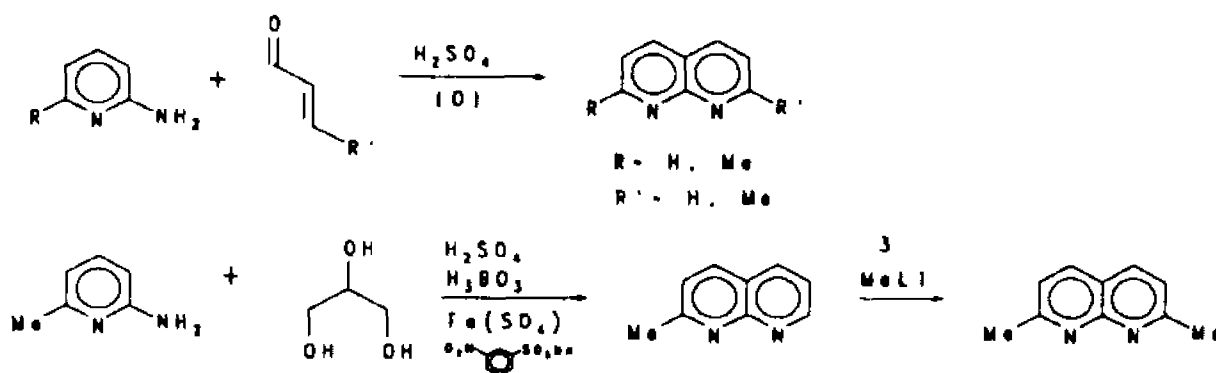
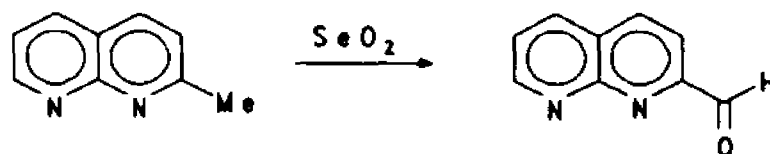


Figure 14. Syntheses of 2,7-Dimethyl-1,8-naphthyridine.

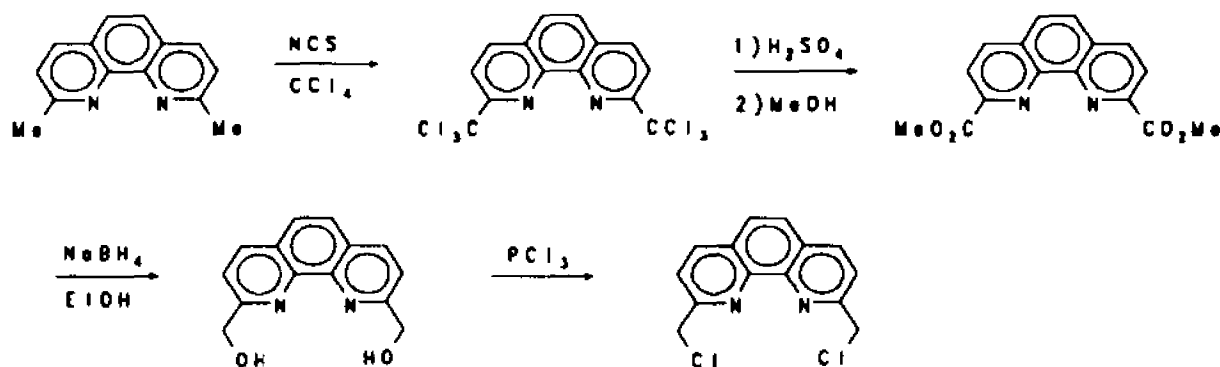
mnap can be prepared in very good yields<sup>198</sup> by the reaction of 2-amino-6-picoline with acrolein (generated in situ from glycerol). Based on reports<sup>227,228</sup> that nap reacts with excess PhLi to give initially 2-phenyl-1,8-naphthyridine and finally 2,7-diphenyl-

1,8-naphthyridine<sup>228</sup> (after oxidation) and that 2,2'-dipyridine was shown<sup>229</sup> to react with MeLi to give 6,6'-dimethyl-2,2'-dipyridine. Newkome and co-workers reacted mnap with three equivalents of MeLi followed by oxidation of the resultant dihydronaphthyridine with  $\text{KMnO}_4$ /acetone to give dmnep in 43% overall yield from 2-amino-6-picoline.<sup>224, 230</sup>

To the best of my knowledge, the only reports of  $\alpha$ -carbon functionalization at the two and seven positions of methyl naps was by the use of  $\text{SeO}_2$ . Thus, Weissenfels and Ulrici described<sup>231</sup> the oxidation of one methyl group of mnap and dmnep to give the mono-aldehydes in 24% and 15% yields, respectively. A later report<sup>232</sup> used  $\text{SeO}_2$  to oxidize 2,4-dimethyl-7-hydroxy-1,8-naphthyridine to the 2,4-dialdehyde in 49% yield. The most recent account<sup>226d</sup> of this oxidation was by Chandler et al. in which dmnep was oxidized to the 2,7-dialdehyde, which was further incorporated into a macrocycle; despite these reports, this oxidation is not easily reproduced.

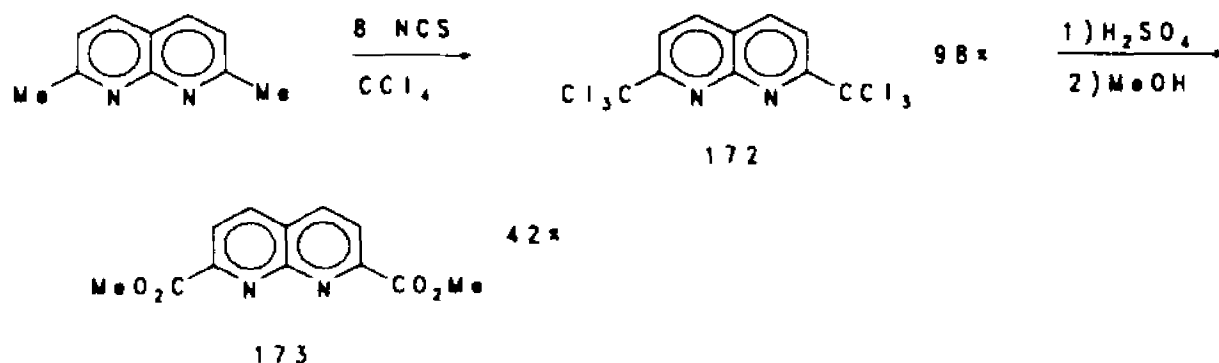


An interesting approach to the methyl functionalization of 2,9-dimethyl-1,10-phenanthroline was reported<sup>233</sup> by Newkome et al. (see Scheme I) in which excess NCS oxidation gave the corresponding bis-trichloromethyl derivative which was hydrolyzed with  $\text{H}_2\text{SO}_4$  followed by MeOH to give the bis-methyl ester. Subsequent reduction with  $\text{NaBH}_4$ /EtOH followed by treatment with  $\text{PCl}_3/\text{CHCl}_3$  gave the desired bis-chloromethyl derivative in 65% overall yield. Using this approach on dmnep, the bis-trichloromethyl derivative **172** was obtained in 98% yield.<sup>224</sup> Unfortunately, subsequent treatment with  $\text{H}_2\text{SO}_4$  followed by MeOH<sup>234</sup> gave only 42% of diester **173**



Scheme I. Functionalization of 2,9-Dimethyl-1,10-phenanthroline.

along with **172** and 2-trichloromethyl-7-methoxycarbonyl-1,8-naphthyridine.<sup>224</sup>



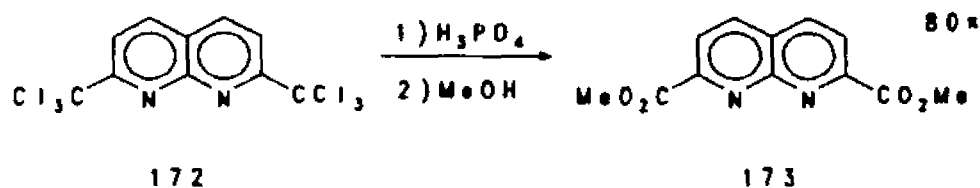
## Results

### Functionalization of 2,7-dimethyl-1,8-naphthyridine

Attempts to functionalize dmnap using two equivalents of NCS<sup>235</sup> gave a mixture of at least seven products which were isolated by column chromatography (with difficulty), none of which were formed in greater than 10% yield; attempted oxidation of dmnap with  $\text{KMnO}_4$  gave starting material. In a continuation of the above scheme, since the treatment of **172** with  $\text{H}_2\text{SO}_4$  at 110 °C gave incomplete reaction, higher temperatures were tried in an effort to force the reaction to completion but no organic soluble material was obtained. On the assumption that ring sulfonation may have occurred,  $\text{H}_3\text{PO}_4$  was chosen for the hydrolysis in an attempt to eliminate this

possibility. As predicted, treatment of **172** with  $\text{H}_3\text{PO}_4$  at  $\approx 170^\circ\text{C}$  followed by MeOH gave diester **173** in 80% yield.

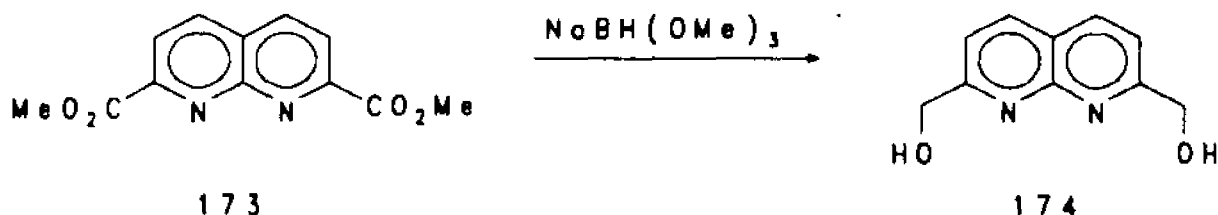
Although  $\text{NaBH}_4$  is not generally used to reduce esters, Brown and Rapoport



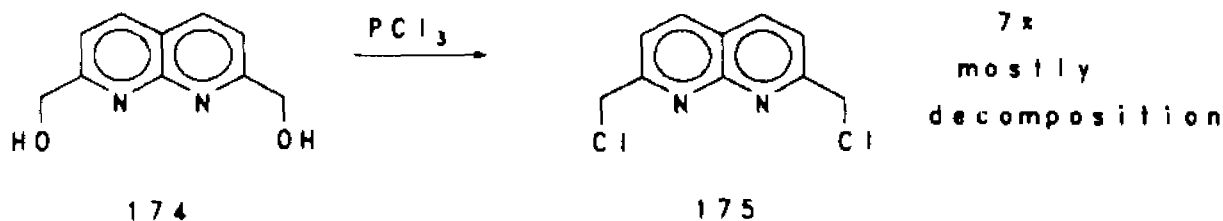
reported<sup>236</sup> that a large excess (10 molar equivalents) of the reagent can be used to reduce aromatic esters in high yields. But when **173** was treated with an excess of  $\text{NaBH}_4$ , diverse products were formed due to ring reduction. The  $^1\text{H}$  NMR spectrum of the mixture showed peaks ranging from the aromatic to alkenyl to aliphatic regions. Using only one equivalent of  $\text{NaBH}_4$  gave the same results and lowering the temperature ( $-40$  and  $-25^\circ\text{C}$ ) gave less ring reduction but also less ester reduction. Although  $\text{NaBH}_4$  has not been reported to reduce aromatic rings, borane does reduce nap above  $0^\circ\text{C}$  to 1,2,3,4-tetrahydro-1,8-naphthyridine in 44% yield.<sup>237</sup> After the first hydride transfer from  $\text{NaBH}_4$ ,  $\text{BH}_3$  is formed which can then complex with nap thereby facilitating the ring reduction.

The reducing reagent of choice therefore was a mono-hydride source which would not produce a Lewis acid hydride product. Brown et al. reported<sup>238</sup> that  $\text{NaBH}(\text{OMe})_3$  reduces aldehydes and acyl chlorides effectively (66-79%) but is a poor reducing agent for ethyl benzoate (33%). Despite this report, reaction of **173** with six equivalents of  $\text{NaBH}(\text{OMe})_3$  in DCM/THF gave diol **174** in 55% yield.<sup>239</sup>

Although diol **174** has great potential for ligand modification and is in itself a tetradentate ligand, the seemingly trivial conversion of **174** to the bis-chloromethyl

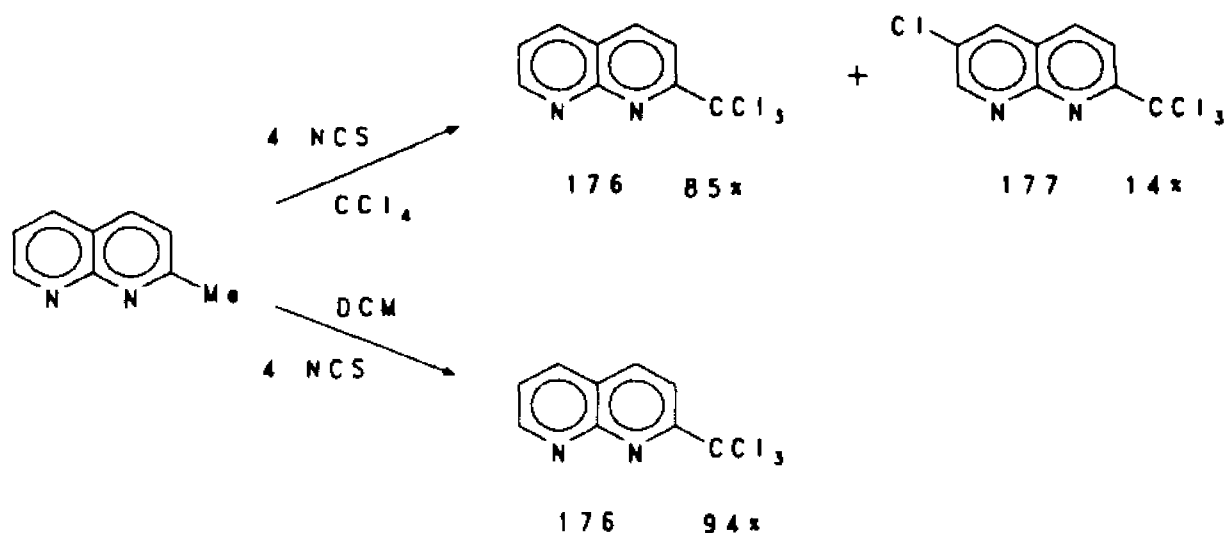


derivative **175** was attempted. Reaction of **174** with  $\text{PCl}_3$  in  $\text{CHCl}_3$  did give **175**, but in only 7% yield with much decomposition. Because **175** is a relatively stable compound and can be stored for long periods, it appears that the acidic reaction conditions cause decomposition of the diol before the chlorination can occur;<sup>240</sup>  $\text{SOCl}_2$  and concentrated  $\text{HCl}$  both gave decomposition. Several neutral chlorinating reagents were tried ( $\text{PPh}_3/\text{CCl}_4$ ,<sup>241</sup>  $\text{NCS}/\text{SEt}_2$ ,<sup>242</sup> treatment of the unquenched reduction mixture with  $\text{PCl}_3$  or methanesulfonyl chloride), all to no avail.

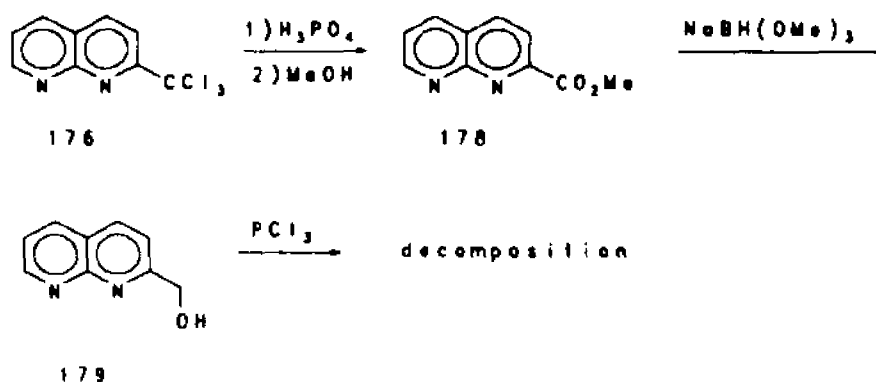


### Functionalization of 2-methyl-1,8-naphthyridine

The reaction of mnap with one equivalent of  $\text{NCS}$  gave a mixture of products and was inappropriate for methyl functionalization. Therefore the same sequence, as was used for dmnep, was attempted with mnap. Treatment of mnap with four equivalents of  $\text{NCS}$  in refluxing  $\text{CCl}_4$  gave the desired 2-trichloromethyl-1,8-naphthyridine (**176**) in 85% yield along with 6-chloro-2-trichloromethyl-1,8-naphthyridine (**177**) as determined by its  $^1\text{H}$  NMR spectrum. Using a more selective solvent (DCM) for the reaction increased the yield of **176** to 94% with only a trace of **177** being formed.



Treatment of 176 with  $\text{H}_3\text{PO}_4$  at  $140^\circ\text{C}$  followed by refluxing in MeOH gave 2-methoxycarbonyl-1,8-naphthyridine (178) in 78% yield. Although attempts to reduce 178 with  $\text{NaBH}_4$  again gave ring reduction, the use of  $\text{NaBH}(\text{OMe})_3$  afforded 2-hydroxymethyl-1,8-naphthyridine (179) in 59% yield. Attempts to chlorinate 179 under acidic conditions, as in the case of 174, also gave decomposition of the alcohol.



Before I discovered the hydrolysis of 172 and 176 with  $\text{H}_3\text{PO}_4$ , basic hydrolysis with  $\text{KOH}/\text{EtOH}$  was attempted based on the proposed mechanism shown in Figure 15. However, under these conditions, the first reaction which takes place is the displacement of the entire trichloromethyl group in a nucleophilic heteroaromatic



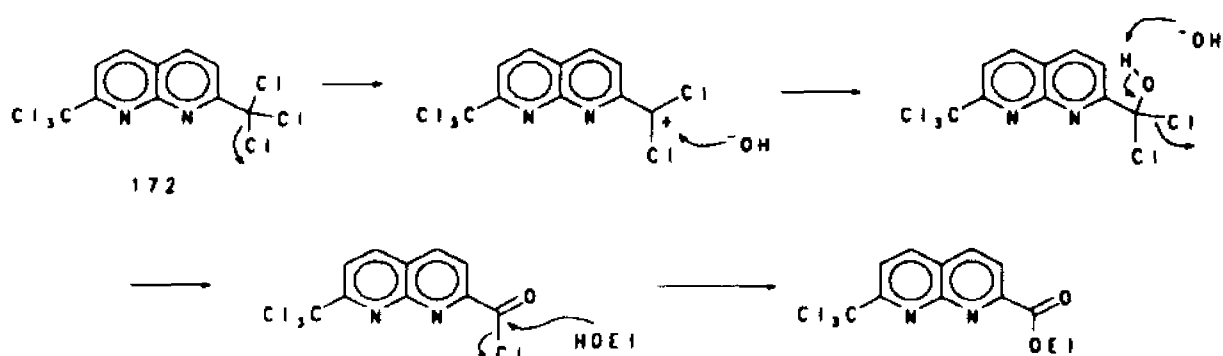
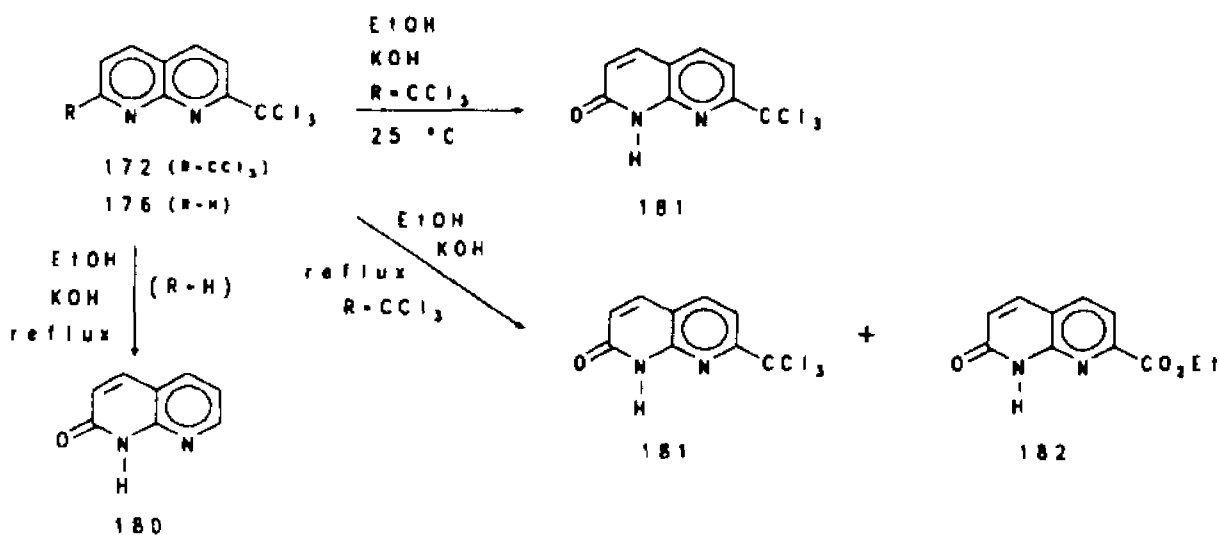


Figure 15. Proposed Mechanism for the Basic Hydrolysis of bis(2,7-Trichloromethyl)-1,8-naphthyridine.

substitution reaction to give a 2-hydroxy group. Thus, from **176**, 1,8-naphthyridin-2-one (**180**) was obtained as the sole product, and from **172**, depending on the reaction conditions, either 7-trichloromethyl-1,8-naphthyridin-2-one (**181**) (25 °C) or its hydrolysis product 7-ethoxycarbonyl-1,8-naphthyridin-2-one (**182**) (reflux) was



formed. The remaining heteroaromatic rings in **181** and **182** are not as electron-deficient as in **172**, thus the second CCl<sub>3</sub> group is not displaced. This type of reaction has been reported for 1,3,5-triazines<sup>243</sup> and for quinazolines<sup>244</sup> but this is the first

example in which a trichloromethyl group acts as a leaving group in a heterocyclic ring possessing only one heteroatom. This reaction is not totally unexpected and is analogous to the haloform reaction for  $\alpha,\alpha,\alpha$ -trihaloketones as shown in Figure 16.

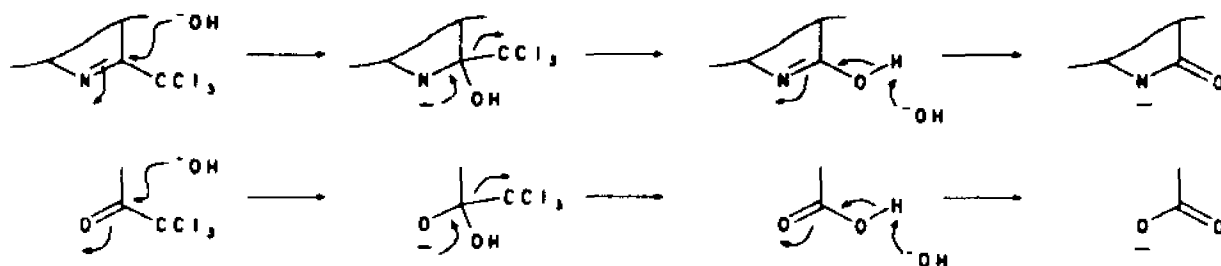


Figure 16. Proposed Mechanism for the Reaction of 2-(Trichloromethyl)-1,8-naphthyridine with KOH and Comparison to the Haloform Reaction.

### NMR Spectroscopy

The  $^1\text{H}$  NMR spectrum of **172** was previously incorrectly reported<sup>224</sup> and so the correct values are reported here. Both **172** and **173** exhibit downfield shifts of the aromatic resonances due to the electron-withdrawing  $\text{CCl}_3$  and  $\text{CO}_2\text{Me}$  moieties, respectively. Diol **174** showed a resonance at 5.01 ppm due to the  $\text{CH}_2$  group which shifted slightly upfield in **175** to 4.9 ppm. The mono-substituted derivatives displayed similar shifts.

For the naphthyridin-2-one derivatives **181** and **182**, the 3-napH shifts were both shifted upfield to 6.79 ppm. This is due to the predominance of the lactam resonance form which causes a shift of the 3-napH into the vinyl region.

Most of the  $^{13}\text{C}$  NMR spectral resonances were easily assigned by comparison to the spectrum of 1,8-naphthyridine.<sup>245</sup> However, for **181** and **182**, the assignments for C3 and C6 were not straightforward. Shift constants for these carbons were calculated based on those derivatives (both mono- and di-substituted) which could be unequivocally assigned. Important to note is that, in 2-pyridone, the greatest shift

difference in comparison to pyridine is in the 5-pyrC (para) which is shifted upfield by 16.9 ppm.<sup>246</sup> Based on this fact, in the spectrum of 1,8-naphthyridin-2-one (**180**), the signal at 118.6 ppm was assigned to C6. This lead to an assignment of the resonances at 113.4 and 118.8 ppm in **181** and **182**, respectively, to C6.

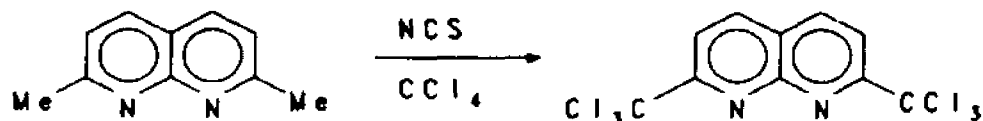
### IR Spectroscopy

The most important absorptions in the IR spectra are those of the NH and C=O stretches in **181** (3434 and 1663  $\text{cm}^{-1}$ ) and **182** (3425 and 1659  $\text{cm}^{-1}$ ) which indicate their "lactam" character.

### Experimental

**General Comments** are found on page 65 in Chapter 1.

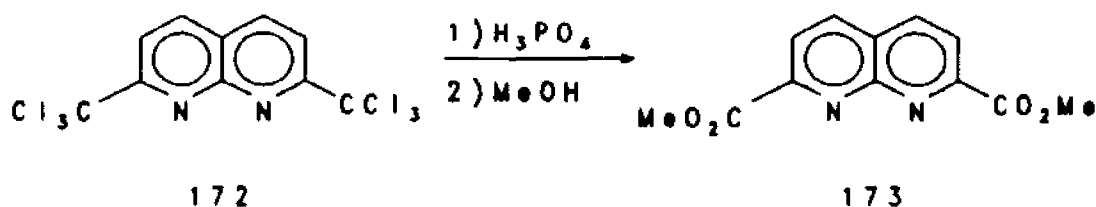
**Reagents.** Unless otherwise noted, all reagents and solvents utilized were of reagent grade and no further purification was undertaken. 2-Methyl- and 2,7-dimethyl-1,8-naphthyridine were prepared by the method of Newkome et al.<sup>224,230</sup>



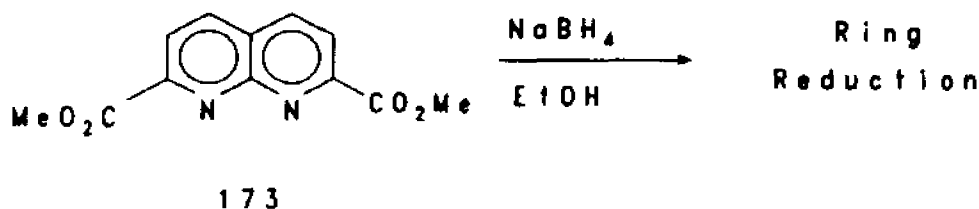
172

**2,7-Bis(trichloromethyl)-1,8-naphthyridine (172)** was prepared from dmnap (89%) by a previously reported procedure<sup>224</sup>: 6.69 g; mp 234-236 °C ( $\text{C}_6\text{H}_{12}$ ) (lit.<sup>224</sup> mp 233-234 °C);  $^1\text{H}$  NMR  $\delta$  8.28 (d, 3-napH,  $J_{3,4} = 8.7$  Hz, 1H), 8.47 (d, 4-napH,  $J_{3,4} = 8.7$  Hz, 1H);  $^{13}\text{C}$  NMR  $\delta$  95.3 ( $\text{CCl}_3$ ), 118.8 (C3), 121.0 (C4a), 137.3 (C4), 149.9 (C8a), 160.4 (C2); MS  $m/e$  364 (6), 333 (21), 331 (67), 329 (100), 327 (64), 294 (33), 292 (21), 222 (11); IR (KBr) 1605, 1549, 1495, 876, 826, 772  $\text{cm}^{-1}$ ; Anal. Calcd for

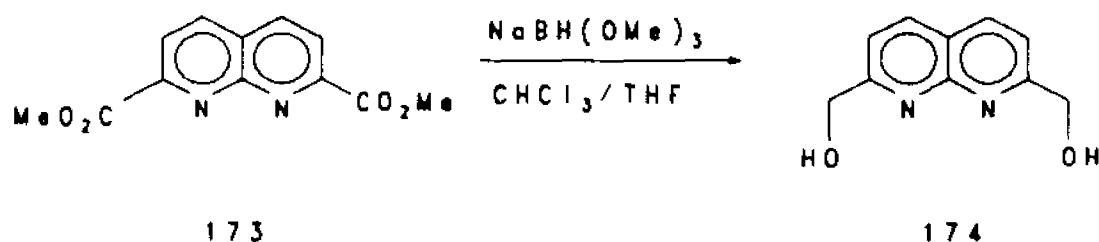
$C_{10}H_4N_2Cl_6$ : C, 32.92; H, 1.10; N, 7.68; Cl, 58.30. Found: C, 32.76; H, 1.16; N, 7.51; Cl, 57.97.



**2,7-Bis(methoxycarbonyl)-1,8-naphthyridine (173).** A solution of 2,7-bis(trichloromethyl)-1,8-naphthyridine (**172**) (7.00 g, 19.1 mmol) in 85%  $\text{H}_3\text{PO}_4$  (25 mL) was heated to 160-170 °C. After 3 h (all of **172** had dissolved) the solution was cooled to 25 °C and MeOH (150 mL) was carefully added. After refluxing for 12 h, most of the MeOH was removed in vacuo and  $\text{CHCl}_3$  (150 mL) and saturated aqueous  $\text{Na}_2\text{CO}_3$  were carefully added. The solution was stirred vigorously for 15 min and then the organic layer was separated, dried over anhydrous  $\text{MgSO}_4$ , filtered, and the  $\text{CHCl}_3$  removed in vacuo to give (80%) diester **173**: 3.76 g; mp 215-217 °C (dec) (lit<sup>224</sup> mp 212-218 °C);  $^1\text{H}$  NMR  $\delta$  4.08 (s,  $\text{CH}_3$ , 3H), 8.34 (d, 3-napH,  $J_{3,4} = 8.4$  Hz, 1H), 8.46 (d, 4-napH,  $J_{3,4} = 8.4$  Hz, 1H);  $^{13}\text{C}$  NMR  $\delta$  52.9 ( $\text{CH}_3$ ), 123.3 (C3), 125.3 (C4a), 138.4 (C4), 152.2 (C2), 154.3 (C8a), 165.4 (CO); MS 246 (2), 216 (30), 215 (5), 188 (100), 187 (24), 157 (5), 156 (40), 128 (67); IR (KBr) 1709, 1381, 1136, 872, 772  $\text{cm}^{-1}$ ; Anal. Calcd for  $\text{C}_{12}\text{H}_{10}\text{N}_2\text{O}_4$ : C, 58.54; H, 4.09; N, 11.38. Found: C, 58.66; H, 4.09; N, 11.09.

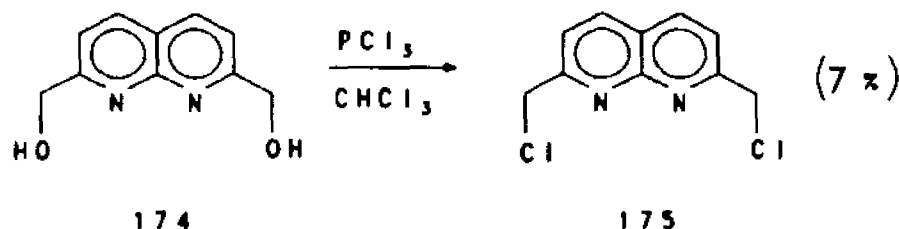


**Attempted Reduction of 2,7-Bis(methoxycarbonyl)-1,8-naphthyridine with  $\text{NaBH}_4$ .** A solution of  $\text{NaBH}_4$  (100 mg, 2.6 mmol) and diester **173** (440 mg, 1.8 mmol) in EtOH (25 mL) was stirred for 1 h at 25 °C. The EtOH was then removed and  $\text{H}_2\text{O}$  (25 mL) added. Continuous extraction with  $\text{CHCl}_3$  for 12 h afforded (12%) diol **174**, after recrystallization from benzene/ $\text{CHCl}_3$ . The majority of the recovered material was comprised of ring reduced products, as determined by  $^1\text{H}$  NMR which contained a vast array of aliphatic and vinyl resonances and very little in the aromatic region. Attempts using  $\text{NaBH}_4$  at lower temperatures (-25 °C and -40 °C) gave diminished ring-reduction, however, the ester reduction was also retarded to such an extent that this was not a viable method.

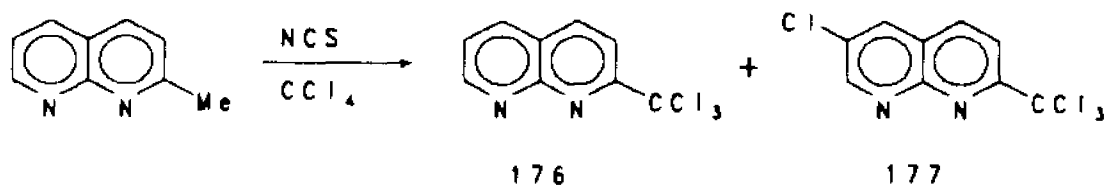


**2,7-Bis(hydroxymethyl)-1,8-naphthyridine (174).** A solution of sodium trimethoxyborohydride (250 mg, 1.95 mmol) in THF (10 mL) was added to a stirred solution of diester **173** (78 mg, 317  $\mu\text{mol}$ ) in  $\text{CH}_2\text{Cl}_2$  (10 mL). The solution was maintained at 25 °C for 1 h after which the solvents were removed in vacuo. The remaining solid was dissolved in saturated aqueous  $\text{NaHCO}_3$  (10 mL), then the water was removed in vacuo. The resulting solid was extracted with hot EtOH (3X, 20 mL) and the EtOH removed in vacuo; extraction of the resultant solid with  $\text{CH}_2\text{Cl}_2$  and removal of the solvent in vacuo gave (55%)<sup>239</sup> diol **174**: 33 mg; mp 143-145 °C ( $\text{CH}_3\text{CN}$ );  $^1\text{H}$  NMR  $\delta$  1.61 (bs, OH, 1H), 5.01 (s,  $\text{CH}_2$ , 2H), 7.48 (d, 3-napH,  $J_{3,4}$  = 8.3 Hz, 1H), 8.21 (d, 4-napH,  $J_{3,4}$  = 8.3 Hz, 1H);  $^{13}\text{C}$  NMR ( $\text{CD}_3\text{OD}$ )  $\delta$  66.2 ( $\text{CH}_2$ ),

120.9 (C3), 122.5 (C4a), 139.6 (C4), 167.2 (C2); (C8a was not observed using a 20 second pulse delay); IR (KBr) 3322, 1609, 1433, 1071, 858, 804, 785  $\text{cm}^{-1}$ ; MS  $m/e$  190 (51), 189 (100), 172 (58), 161 (49), 143 (73), 131 (20); Anal. Calcd for  $\text{C}_{10}\text{H}_{10}\text{N}_2\text{O}_2$ : C, 63.15; H, 5.30; N, 14.73. Found: C, 63.20; H, 5.36; N, 14.72.



**Chlorination of 2,7-Bis(hydroxymethyl)-1,8-naphthyridine with  $\text{PCl}_3$ .**  $\text{PCl}_3$  (0.75 mL, 8.6 mmol) was added dropwise to a stirred solution of diol **174** (102 mg, 0.54 mmol) in  $\text{CHCl}_3$ . After refluxing for 30 min, the  $\text{CHCl}_3$  was removed in vacuo, and the resulting oil neutralized with saturated aqueous  $\text{Na}_2\text{CO}_3$  and then extracted with  $\text{CH}_2\text{Cl}_2$ . The solution was dried over anhydrous  $\text{MgSO}_4$ , filtered and the  $\text{CH}_2\text{Cl}_2$  removed to give traces of a white solid, which proved to be a mixture of 2,7-bis(chloromethyl)-1,8-naphthyridine (**175**) (85%) and diol **174** (15%) as determined by  $^1\text{H}$  NMR. However, only 8 mg of solid was recovered (7% yield of **175**). A considerable amount of decomposition was noted in the reaction.



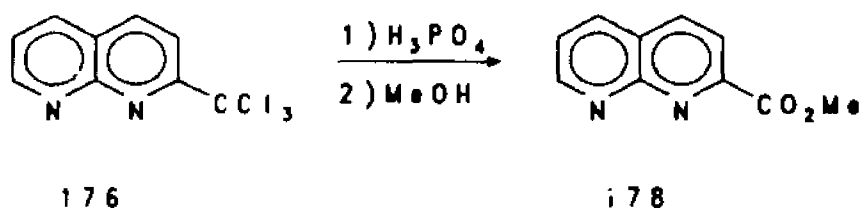
**2-Trichloromethyl-1,8-naphthyridine (172).** A stirred solution of 2-methyl-1,8-naphthyridine (3.0 g, 20.8 mmol) and *N*-chlorosuccinimide (NCS) (11.10 g, 83.0

mmol) in  $\text{CCl}_4$  (200 mL) was refluxed and benzoyl peroxide (1-3 mg) was added every 30 min for the first 2 h; the solution was refluxed for an additional 20 h. The solvent was removed in vacuo and the solid residue dissolved in  $\text{CHCl}_3$  which was washed twice with saturated aqueous  $\text{Na}_2\text{CO}_3$ . The  $\text{CHCl}_3$  solution was dried over anhydrous  $\text{MgSO}_4$ , filtered, and the solvent removed in vacuo to give a light yellow solid, which was purified by dry-flash chromatography using  $\text{CHCl}_3$ , as eluant, collecting two fractions:

**Fraction 1: 6-Chloro-2-trichloromethyl-1,8-naphthyridine (177):** 800 mg; 14%; mp 128-130 °C (dec);  $^1\text{H}$  NMR  $\delta$  8.25 (d, 5-napH,  $J_{5,7} = 2.6$  Hz, 1H), 8.26 (d, 3-napH,  $J_{3,4} = 8.7$  Hz, 1H), 8.35 (d, 4-napH,  $J_{3,4} = 8.7$  Hz, 1H), 9.11 (bs, 7-napH, 1H);  $^{13}\text{C}$  NMR  $\delta$  97.0 ( $\text{CCl}_3$ ), 119.8 (C3), 122.9 (C4a), 131.4 (C6), 134.5 (C4), 138.6 (C5), 151.8 (C8a), 154.3 (C7), 160.7 (C2); IR (KBr) 1595, 1549, 849, 829, 772  $\text{cm}^{-1}$ ; MS  $m/e$  284 (7), 282 (14), 280 (10), 249 (32), 247 (100), 249 (96), 210 (15); Anal. Calcd for  $\text{C}_9\text{H}_4\text{N}_2\text{Cl}_4$ : C, 38.34; H, 1.43; N, 9.94; Cl, 50.30. Found: C, 38.24; H, 1.48; N, 9.77; Cl, 50.13.

**Fraction 2: 2-trichloromethyl-1,8-naphthyridine (176):** 4.38 g; 85%; mp 174-176 °C (dec);  $^1\text{H}$  NMR  $\delta$  7.61 (dd, 6-napH,  $J_{5,6} = 8.2$  Hz,  $J_{6,7} = 8.1$  Hz, 1H), 8.19 (d, 3-napH,  $J_{3,4} = 8.7$  Hz, 1H), 8.29 (dd, 5-napH,  $J_{5,6} = 8.2$ ,  $J_{5,7} = 2.0$  Hz, 1H), 8.40 (d, 4-napH,  $J_{3,4} = 8.7$  Hz, 1H), 9.23 (dd, 7-napH,  $J_{6,7} = 4.2$ ,  $J_{5,7} = 2.0$  Hz, 1H);  $^{13}\text{C}$  NMR  $\delta$  97.3 ( $\text{CCl}_3$ ), 118.7 (C3), 122.7 (C4a), 123.7 (C6), 136.7 (C4), 139.4 (C5), 153.7 (C8a), 154.9 (C7), 160.4 (C2); MS 248 (18), 246 (19), 213 (68), 211 (100), 176 (21), 129 (14); IR (KBr) 1599, 1555, 824, 785, 768, 762  $\text{cm}^{-1}$ ; Anal. Calcd for  $\text{C}_9\text{H}_5\text{N}_2\text{Cl}_3$ : C, 43.67; H, 2.04; N, 11.32; Cl, 42.97. Found: C, 43.75; H, 1.88; N, 11.16; Cl, 42.84.

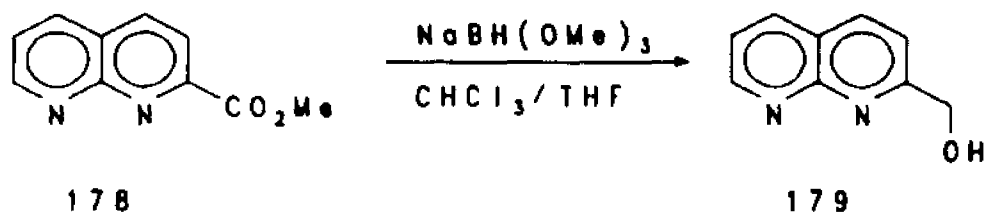
In an attempt to avoid ring chlorination the following procedure was used. A stirred solution of 2-methyl-1,8-naphthyridine (1.0 g, 6.9 mmol) and NCS (3.7 g, 27.2 mmol) in  $\text{CH}_2\text{Cl}_2$  (100 mL) was refluxed and a catalytic amount of azoisobutyronitrile (AIBN) was added; additional AIBN ( $\approx 5$  mg) was added every hour for 4 h. The solution was refluxed for an additional 12 h and then cooled, washed twice with saturated aqueous  $\text{Na}_2\text{CO}_3$ , dried over anhydrous  $\text{MgSO}_4$ , filtered, and the solvent removed in vacuo to give (94%) **176**, as a light yellow solid. Traces of ring chlorinated product were detected (<5%).



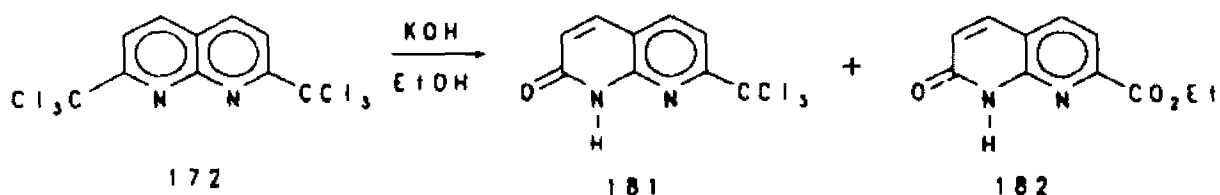
**2-Methoxycarbonyl-1,8-naphthyridine (178).** A stirred mixture of **176** (1.6 g, 6.5 mmol) and 85%  $\text{H}_3\text{PO}_4$  (10 mL) was heated to 140 °C for 3 h. After cooling, anhydrous MeOH (25 mL) was carefully added and the mixture refluxed for 12 h. Most of the MeOH was removed and the remaining slurry was treated with saturated aqueous  $\text{Na}_2\text{CO}_3$ . Extraction of the basic solution with  $\text{CH}_2\text{Cl}_2$ , followed by drying over anhydrous  $\text{MgSO}_4$ , and removal of the  $\text{CH}_2\text{Cl}_2$  gave (78%) **178**, as a tan solid: 950 mg; mp 146-150 °C;  $^1\text{H}$  NMR  $\delta$  4.08 (s,  $\text{CH}_3$ , 3H), 7.59 (dd, 6-napH,  $J_{5,6} = 8.2$ ,  $J_{6,7} = 4.2$  Hz, 1H), 8.26 (d, 3-napH,  $J_{3,4} = 9.8$  Hz, 1H), 8.27 (dd, 5-napH,  $J_{5,6} = 8.2$ ,  $J_{5,7} = 2.0$  Hz, 1H), 8.40 (d, 4-napH,  $J_{3,4} = 9.8$  Hz, 1H), 9.24 (dd, 7-napH,  $J_{6,7} = 4.2$ ,  $J_{5,7} = 2.0$  Hz, 1H);  $^{13}\text{C}$  NMR  $\delta$  52.6 ( $\text{CH}_3$ ), 121.6 (C6), 123.4 (C3), 124.0 (C4a), 136.6 (C5), 138.5 (C4), 150.6 (C8a), 154.6 (C7), 155.0 (C2), 165.4 (CO); MS  $m/e$



158 (22), 130 (100), 129 (40); IR (KBr) 1709, 1601, 1451, 1318, 1235, 1140, 870, 801, 774  $\text{cm}^{-1}$ ; Anal. Calcd for  $\text{C}_{10}\text{H}_8\text{N}_2\text{O}_2$ : C, 63.83; H, 4.28; N, 14.89. Found: C, 63.64; H, 4.41; N, 14.69.



**2-Hydroxymethyl-1,8-naphthyridine (179).** A solution of sodium trimethoxyborohydride (379 mg, 2.97 mmol) in THF (10 mL) was added to a stirred solution of ester **178** (184 mg, 979  $\mu\text{mol}$ ) in  $\text{CH}_2\text{Cl}_2$  (10 mL). The solution was maintained at 25  $^\circ\text{C}$  for 1 h, after which the solvents were removed in vacuo. The remaining solid was dissolved in saturated aqueous  $\text{NaHCO}_3$  (10 mL) and the water removed in vacuo. The resulting solid was then extracted with hot EtOH (3X, 20 mL) and the combined EtOH extract was concentrated in vacuo to give a solid, which was purified by dry-flash chromatography eluting first with EtOAc, followed by 3:2 EtOAc/EtOH to give (59%) alcohol **179**: 93 mg; mp 99-100  $^\circ\text{C}$  (benzene/ $\text{CHCl}_3$ );  $^1\text{H}$  NMR  $\delta$  4.40 (b, OH, 1H), 5.01 (s,  $\text{CH}_2$ , 2H), 7.46 (d, 3-napH,  $J_{3,4} = 8.4$  Hz, 1H), 7.51 (dd, 6-napH,  $J_{5,6} = 8.1$ ,  $J_{6,7} = 4.3$  Hz, 1H), 8.20 (d, 4-napH,  $J_{3,4} = 8.4$  Hz, 1H), 8.22 (dd, 5-napH,  $J_{5,6} = 8.1$ ,  $J_{5,7} = 2.0$  Hz, 1H), 9.10 (dd, 7-napH,  $J_{6,7} = 4.3$ ,  $J_{5,7} = 2.0$  Hz, 1H);  $^{13}\text{C}$  NMR  $\delta$  64.5 ( $\text{CH}_2$ ), 119.7 (C3), 122.2 (C6), 137.2, 137.9 (C4, C5), 153.7 (C7), 163.9 (C2), (C4a and C8a were not observed with a 4 second delay); IR (KBr) 3412, 1607, 1499, 1080, 848, 808, 777  $\text{cm}^{-1}$ ; Anal. Calcd for  $\text{C}_9\text{H}_8\text{N}_2\text{O}$ : C, 67.49; H, 5.03; N, 17.49. Found: C, 67.25; H, 5.16; N, 17.30.



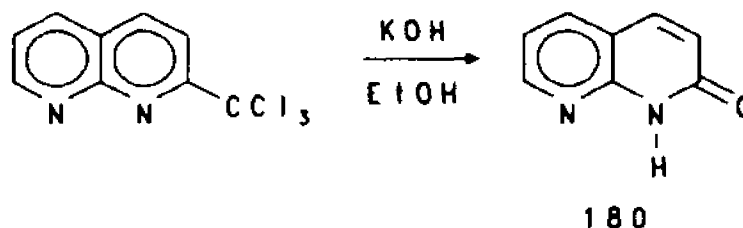
**Reaction of 2,7-Bis(trichloromethyl)-1,8-naphthyridine (172) with KOH in EtOH.** A stirred solution of **172** (254 mg, 696  $\mu\text{mol}$ ) and KOH (474 mg, 8.46 mmol) in EtOH (35 mL) was refluxed for 3 h. The EtOH was then removed in vacuo and saturated aqueous  $\text{NaHCO}_3$  (10 mL) was added. The aqueous solution was extracted with  $\text{CHCl}_3$  (3X, 20 mL) and the combined organic solution was dried over anhydrous  $\text{MgSO}_4$ , filtered, and the solvent removed in vacuo to give a brown solid, which was purified using dry-flash chromatography eluting initially with  $\text{CHCl}_3$ , followed by 1:1  $\text{CHCl}_3/\text{EtOAc}$  to give 2 fractions:

**Fraction 1: 7-trichloromethyl-1,8-naphthyridin-2-one (181):** (73 mg, 40%); mp 201-202  $^\circ\text{C}$  (dec);  $^1\text{H}$  NMR  $\delta$  6.79 (d, 3-napH,  $J_{3,4} = 9.6$  Hz, 1H), 7.74 (d, 4-napH,  $J_{3,4} = 9.6$  Hz, 1H), 7.86 (d, 6-napH,  $J_{5,6} = 8.2$  Hz, 1H), 8.03 (d, 5-napH,  $J_{5,6} = 8.2$  Hz, 1H), 9.56 (bs, OH, 1H);  $^{13}\text{C}$  NMR ( $\text{Me}_2\text{SO}-d_6$ )  $\delta$  96.8 ( $\text{CCl}_3$ ), 113.4 (C6), 115.8 (C4a), 125.3 (C3), 138.2 (C4), 138.9 (C5), 148.9 (C8a), 157.1 (C7), 163.0 (C2); MS  $m/e$  264 (11), 262 (10), 229 (71), 227 (100); IR (KBr) 3434, 1663, 1597, 1547, 870, 824, 762  $\text{cm}^{-1}$ ; Anal. Calcd for  $\text{C}_9\text{H}_5\text{N}_2\text{Cl}_3\text{O}$ : C, 41.02; H, 1.91; N, 10.63; Cl 40.36. Found: C, 41.20; H, 1.87; N, 10.31; Cl, 40.41.

**Fraction 2: 7-ethoxycarbonyl-1,8-naphthyridin-2-one (182):** (26 mg, 17%); mp 207-208  $^\circ\text{C}$  (dec);  $^1\text{H}$  NMR  $\delta$  1.45 (t,  $\text{CH}_3$ ,  $J = 7.1$  Hz, 3H), 4.50 (q,  $\text{CH}_2$ ,  $J = 7.1$  Hz, 2H), 6.79 (d, 3-napH,  $J_{3,4} = 9.6$  Hz, 1 H), 7.74 (d, 4-napH,  $J_{3,4} = 9.6$  Hz, 1H), 7.99 (s, 5,6-napH, 2H), 9.48 (bs, OH, 1H);  $^{13}\text{C}$  NMR ( $\text{Me}_2\text{SO}-d_6$ )  $\delta$  14.0 ( $\text{CH}_3$ ), 61.4

(CH<sub>2</sub>), 117.1 (C4a), 118.8 (C6), 125.4 (C3), 137.8 (C5), 138.4 (C4), 147.4 (C8a), 149.8 (C7), 163.0 (C2), 164.4 (CO); MS *m/e* 218 (30), 173 (7), 146 (100), 145 (30); IR (KBr) 3425, 1730, 1659, 1595, 1547, 1287, 1154, 764 cm<sup>-1</sup>; Anal. Calcd for C<sub>11</sub>H<sub>10</sub>N<sub>2</sub>O<sub>3</sub>: C, 60.55; H, 4.62; N, 12.84. Found: C, 60.53; H, 4.74; N, 12.71.

When the reaction was conducted at 25 °C for 36 h, the formation of **181** was increased to 79% with very little **182** being formed.

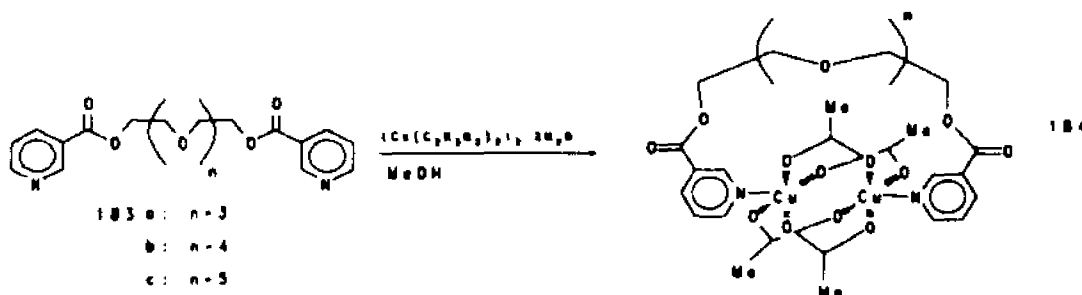


**Reaction of 2-Trichloromethyl-1,8-naphthyridine (176) with KOH in EtOH.** A stirred solution of **176** (268 mg, 1.08 mmol) and KOH (623 mg, 11.1 mmol) in absolute EtOH (20 mL) was refluxed for 3 h. The EtOH was then removed in vacuo and saturated aqueous NaHCO<sub>3</sub> (10 mL) was added. The aqueous solution was extracted with CHCl<sub>3</sub> (3X, 15 mL), the combined organic solution dried over anhydrous MgSO<sub>4</sub>, filtered, and the solvent removed in vacuo to give a brown solid, which was purified using dry-flash chromatography eluting initially with CHCl<sub>3</sub>, followed by 1:1 CHCl<sub>3</sub>/EtOAc to give (61%) 1,8-naphthyridin-2-one (**180**): 96 mg; mp 198-201.5 °C; (lit.<sup>247</sup> mp 198-199 °C, lit.<sup>248</sup> mp 197-198 °C) <sup>13</sup>C NMR δ 115.0 (C4a), 118.6 (C6), 123.8 (C3), 136.4 (C5), 138.8 (C4), 150.0 (C8a), 150.6 (C7), 164.0 (C2); Anal. Calc for C<sub>8</sub>H<sub>6</sub>N<sub>2</sub>O: C, 65.75; H, 4.14; N, 19.17. Found: C, 65.59; H, 4.23; N, 19.10.

## Chapter 4. Synthesis of Metal Paddlanes.<sup>†</sup>

### Introduction

Several attempts have been made to correlate the structural and magnetic properties in dinuclear metal(II) carboxylate complexes.<sup>249</sup> In order to further elucidate the interactions in these species we designed flexible *N,N'*-bidentate ligands (**183**) and attempted construction of macrocyclic copper(II) carboxylate complexes (paddlanes) of the type **184** depicted in Scheme II.



Scheme II. Synthesis of Metal Paddlanes.

In the 1:1 complex of **183** with dimeric copper(II) acetate to form the metal paddlane **184**, variation of the chain length in the ligand (*n* = 3-5), was expected to systematically alter the copper acetate moiety and provide a better insight into the Cu-Cu interaction.

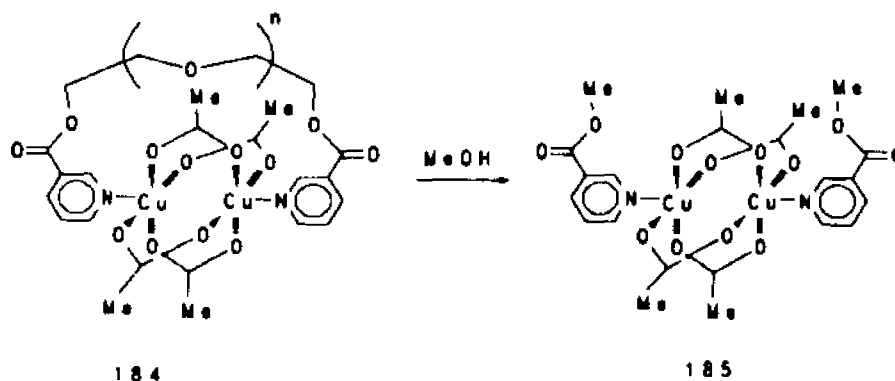
### Results

Reaction of nicotinoyl chloride<sup>250</sup> with an appropriate glycol in benzene gave **183** (ca. 100%), as colorless oils<sup>251</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.42 (dd, 5-pyH, *J*<sub>5,6</sub> = 4.9, *J*<sub>4,5</sub> = 7.9 Hz, 2H), 8.33 (ddd, 4-pyH, *J*<sub>2,4</sub> = *J*<sub>4,6</sub> = 2.0, *J*<sub>4,5</sub> = 7.9 Hz, 2H), 8.78 (dd, 6-pyH, *J*<sub>4,6</sub> = 2.0, *J*<sub>5,6</sub> = 4.9 Hz, 2H), 9.24 (d, 2-pyH, *J* = 2.0 Hz, 2H).<sup>252</sup> An equimolar mixture of **183** and  $[Cu(C_2H_3O_2)_2]_2 \cdot 2H_2O$  in MeOH at 25 °C under high-dilution

<sup>†</sup>Newkome, G. R.; Theriot, K. J.; Gupta, V. K.; Balz, R. N.; Fronczek, F. R. *Inorg. Chim. Acta* **1986**, *114*, 21.

conditions <sup>253</sup> yielded a bluish-green solid (**184**)  $n = 4$ : mp 164-165 °C;  $n = 5$ : mp 118-119 °C.

Although the complexation reaction which leads to **184** was conducted in MeOH, the only crystals obtained from the recrystallization of **184b** ( $n = 4$ ) in MeOH/CHCl<sub>3</sub> was the methyl nicotinate complex of copper acetate **185** [mp > 225 °C (dec)]! The formation of **185** occurred by facile transesterification of the ligand portion of complex **184b** during recrystallization; recrystallizations from aprotic solvents do not give **185**. The fact that transesterification does not occur in the reaction is due to the relatively short reaction time (3 h) compared to recrystallization (1 week). In light of this, the role of chloroform is simply that of a co-crystallization solvent. In addition, the commutation appeared to occur solely on the complexed ligand since attempted transesterifications of non-ligating esters (i.e. benzoate esters) in the presence of copper acetate failed. Because of the mild reaction conditions (25 °C, MeOH/CHCl<sub>3</sub>), participation by copper is not unlikely; however this possibility has not been pursued. Slow evaporation of a MeOH/CHCl<sub>3</sub> solution gave single crystals of **185**. Due to the small amount of material used in the recrystallization ( $\approx 5$  mg), no other products were isolated, nor was the yield determined.



### Crystal Data

Formula weight = 637.5, monoclinic, space group  $P2_1/c$ ,  $a = 8.710(2)$ ,  $b = 18.823(5)$ ,  $c = 8.059(2)$  Å,  $\beta = 92.56(2)^\circ$ ,  $Z = 2$ ,  $D_c = 1.604$  g cm<sup>-3</sup>,  $T = 24$  °C,  $\mu(\text{MoK}\alpha) = 16.77$  cm<sup>-1</sup>,  $R = 0.043$  for 1612 observed data.

Intensity data were collected on an Enraf-Nonius CAD4 diffractometer equipped with MoK $\alpha$  radiation ( $\lambda = 0.71073$  Å) and a graphite monochromator, using a crystal of dimensions 0.14 X 0.32 X 0.42 mm. All data in one quadrant having  $1^\circ < \theta < 25^\circ$  were measured by  $\omega$ - $2\theta$  scans of variable rate. Scan rates varied 0.74-10.00 deg min<sup>-1</sup> in order to measure all significant reflections with  $I \approx 50\sigma(I)$ . Data reduction included corrections for background, decay (23%), Lorentz, and polarization effects, as well as absorption corrections based on  $\psi$  scans of reflections near  $\chi = 90^\circ$ . The minimum relative transmission coefficient was 0.582. A total of 2328 unique data was measured, of which 1612 had  $I > 3\sigma(I)$  and were used in the refinement.

The structure was solved by heavy atom methods and refined by full matrix least squares based on  $F$  with weights  $w = \sigma^{-2}(F_o)$ , using the Enraf-Nonius SDP programs.<sup>254</sup> Nonhydrogen atoms were treated anisotropically; hydrogen atoms were located by difference maps and included as fixed contributions. The maximum residual density in a final difference map was 0.72 eÅ, near Cu.

### Discussion

Selected bond distances are listed in Table XV. The copper acetate dimer structure is observed with methyl nicotinate capping the apical position. There is a center of symmetry between the two copper atoms. The Cu-Cu distance is 2.607(1) Å, which falls within the range of that observed in copper acetate complexes with  $N$ -donor ligands (2.58-2.67 Å).<sup>249c</sup> As well, the Cu-N distance of 2.173(3) Å is also within the

normally observed range (2.08-2.24 Å).<sup>249c</sup> The geometry around copper is distorted tetragonal-pyramidal with the copper atom out of the basal plane of the four oxygens, displaced toward the nitrogen atom, by 0.197(1) Å as compared to similar compounds with a range of 0.19-0.23 Å.<sup>249c</sup> The Cu-O distances average 1.974 Å. In both independent acetate groups, the two C-O distances differ by statistically significant amounts. Since no reason for this difference is readily apparent, it may be indicative of an under-estimation of the uncertainties, or of imperfect decay and absorption corrections. No abnormal intermolecular interactions are observed. An ORTEP drawing of **185** is given in Figure 17.

Table XV. Selected Bond Distances (Å) and Angles (°) for  
 $[\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2]_2 \cdot 2\text{C}_7\text{H}_7\text{NO}_2$ .

Cu-O(1)	1.978(2)	Cu-O(1)-C(1)	123.4(2)
Cu-O(2)	1.975(2)	Cu-O(2)-C(1)	122.5(2)
Cu-O(3)	1.979(3)	Cu-O(3)-C(3)	120.7(3)
Cu-O(4)	1.964(3)	Cu-O(4)-C(3)	125.8(3)
Cu-N(1)	2.173(3)	O(1)-C(1)-O(2)	125.3(3)
Cu-Cu'	2.607(1)	O(3)-C(3)-O(4)	124.8(4)
C(1)-O(1)	1.260(4)]	N(1)-Cu-O(1)	94.5(1)
C(1)-O(2)	1.232(4)	N(1)-Cu-O(2)	96.9(1)
C(3)-O(3)	1.270(5)	N(1)-Cu-O(3)	95.9(1)
C(3)-O(4)	1.229(5)	N(1)-Cu-O(4)	95.6(1)



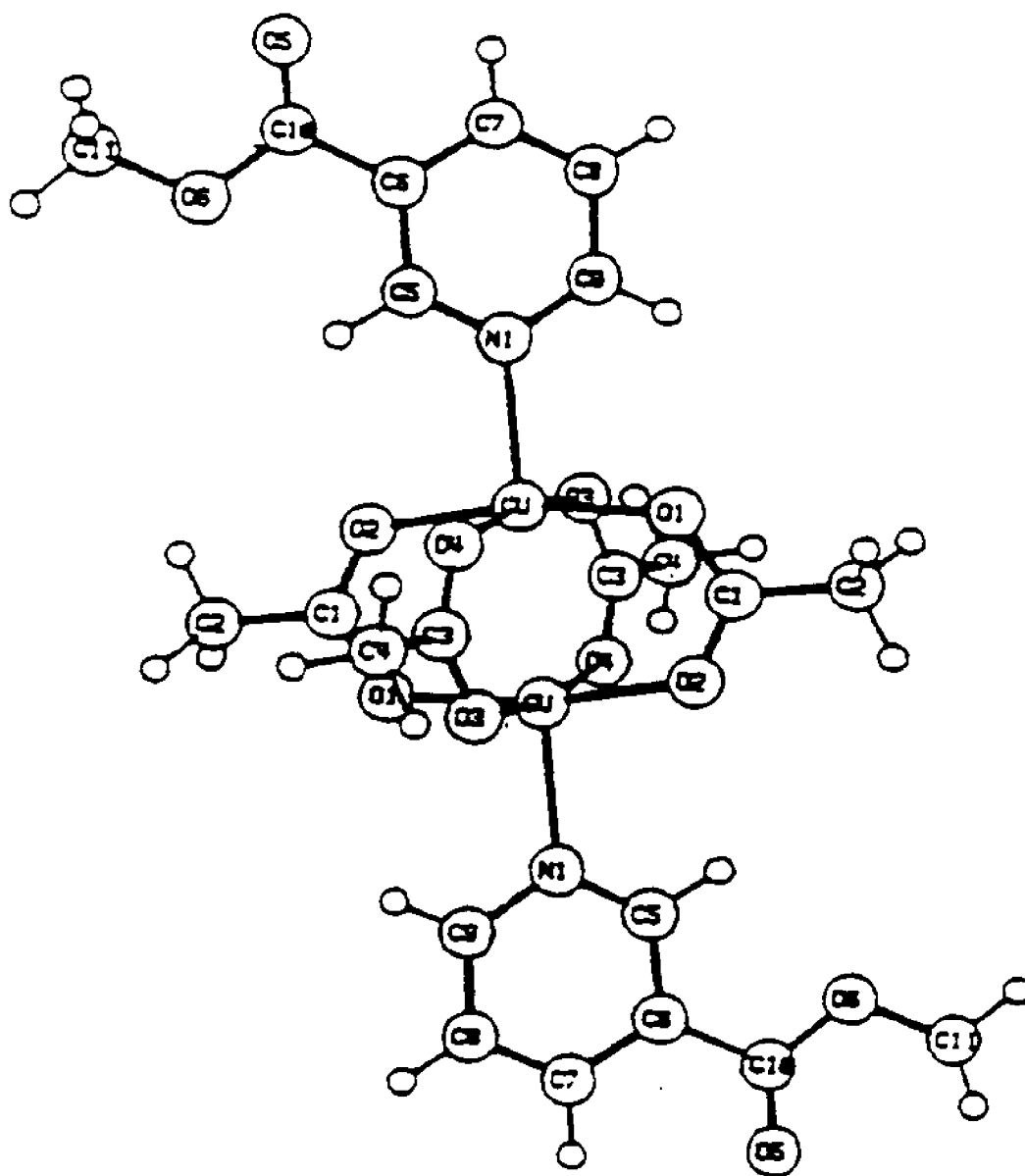


Figure 17. ORTEP Drawing of 185.

## Chapter 5. Hydrogen-Bonding in the Pyridine-Oxalic Acid System<sup>†</sup>

### Introduction

Grigorowsky and Kimen reported<sup>255</sup> a 1:1 adduct between pyridine and oxalic acid in 1945. Reaction of an equimolar mixture of oxalic acid and pyridine would be expected to give pyridinium hydrogen oxalate based on  $pK_a$  data. Our interest in this system was based on a report<sup>256</sup> from our labs of a macrocycle in which pyridine was  $\mu$ -bonded to two different atoms. The 1:1 adduct between pyridine and oxalic acid also has the potential for intramolecular  $\mu$ -bonding of the pyridine moiety with the two acidic protons.

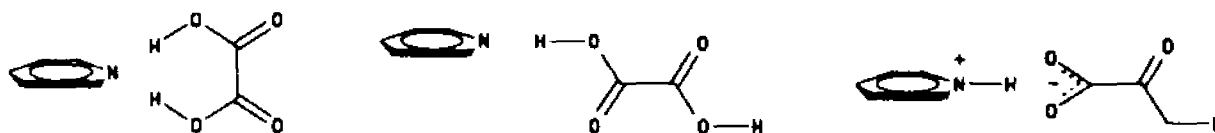


Figure 18. Possible Bonding Modes in the 1:1 Pyridine/oxalic acid System.

An equimolar mixture of pyridine and oxalic acid in MeOH indeed gave a 1:1 salt as shown by combustion analysis. An X-ray crystal structure of the 1:1 salt was undertaken to gain insight into its structure. It was shown that  $\mu$ -bonding was not present and that the 1:1 salt was *not* the expected hydrogen oxalate salt but rather dipyridinium oxalate-oxalic acid (186). Further investigations showed that the product which is formed is dependent on the solvent system used. Thus, when pyridine and oxalic acid were mixed in a 1:1 ratio in 10% MeOH/ $\text{CHCl}_3$  a different salt was formed which was shown to be dipyridinium bis(hydrogen oxalate)-oxalic acid (187)

<sup>†</sup>(a) Newkome, G. R.; Theriot, K. J.; Fronczek, F. R. *Acta Cryst.* **1985**, *C41*, 1642. (b) Newkome, G. R.; Theriot, K. J.; Fronczek, F. R. *Acta Cryst.* **1986**, *C42*, 1539.

by X-ray crystallography.

### Experimental

**Dipyridinium oxalate-oxalic acid.** An equimolar mixture of pyridine and oxalic acid dihydrate in MeOH gave **186** as colorless crystals: mp 426-428 K;  $^1\text{H}$  NMR ( $\text{CD}_3\text{OD}$ )  $\delta$  7.72-7.89 (m, 3-pyH, 2H), 8.30 (tt, 4-pyH,  $J_{3,4} = 7.7$ ,  $J_{2,4} = 1.7$  Hz, 1H), 8.76 (dd, 2-pyH,  $J_{2,3} = 4.7$  Hz, 2H). A colorless tabular crystal of dimensions 0.16 X 0.42 X 0.45 mm was mounted on a capillary. Space-group determination was done by successful refinement of a centrosymmetric model. Data were collected on an Enraf-Nonius CAD-4 diffractometer with a graphite monochromator using Mo  $K\alpha$  radiation. Cell dimensions were obtained from setting angles of 25 reflections,  $24 < 2\theta < 30^\circ$ . Data collection was by  $\omega$ - $2\theta$  scans designed for  $I=50\sigma(I)$ . Scan rates varied  $0.53$ - $5.0^\circ \text{ min}^{-1}$ . Reflections having  $1 < \theta < 30^\circ$ ,  $0 \leq h \leq 5$ ,  $-11 \leq k \leq 11$ ,  $-15 \leq l \leq 15$  were measured and corrected for background, Lorentz, and polarization effects. Three standard reflections were used with  $\pm 2.5\%$  random variation. The structure was solved using *MULTAN*<sup>257</sup> by phasing in  $P\bar{1}$  space group from fragments recognized in  $E$  maps in  $P\bar{1}$ . Refinement was done by full-matrix least squares (based on  $F$ ) using data for which  $I > 3\sigma(I)$  (765 unobserved reflections),  $w=[\sigma^2(F) + 0.02F^2]^{-1}$ , with Enraf-Nonius *SDP* package.<sup>258</sup> Non-H atoms were refined anisotropically; H-atoms were located by  $\Delta F$  and were refined isotropically. Final  $R = 0.041$ ,  $R_w = 0.057$ ,  $S = 1.993$  for 138 variables, with the largest residual densities of 0.33 and 0.36  $\text{e}\text{\AA}^{-3}$  on oxalic acid and oxalate centers. The extinction coefficient was  $3.3(7) \times 10^{-6}$  with a maximum shift in the final cycle of  $0.01\sigma$ . Atomic coordinates and equivalent isotropic thermal parameters can be found in reference 259a. Formula:  $2\text{C}_5\text{H}_6\text{N}^+\cdot\text{C}_2\text{H}_2\text{O}_4$ ,  $M_r = 338.3$ , triclinic,  $P\bar{1}$ ,  $a = 3.999(2)$ ,  $b = 8.439(4)$ ,  $c =$

11.319(3) Å,  $\alpha = 77.96(3)$ ,  $\beta = 88.64(2)$ ,  $\gamma = 82.69(3)^\circ$ ,  $V = 370.5(4) \text{ Å}^3$ ,  $Z = 1$ ,  $D_x = 1.516 \text{ g cm}^{-3}$ , Mo  $K\alpha$ ,  $\lambda = 0.71073 \text{ Å}$ ,  $\mu = 1.18 \text{ cm}^{-1}$ ,  $F(000) = 176$ ,  $T = 301 \text{ K}$ ,  $R = 0.041$  for 1390 observations (of 2155 unique data).

**Dipyridinium bis(hydrogen oxalate)-oxalic acid.** Pyridine (630 mg, 8.0 mmol) in  $\text{CHCl}_3$  (10 mL) was added to a solution of oxalic acid dihydrate (1.0 g, 8.0 mmol) in 10% MeOH/ $\text{CHCl}_3$ ; slow evaporation yielded colorless prisms of **187**. A crystal of dimensions 0.10 X 0.26 X 0.56 mm was sealed in a capillary. The space group was determined from the systematic absences  $h0l$  with  $h+l$  odd,  $0k0$  with  $k$  odd. The cell dimensions were ascertained from setting angles of 25 reflections having  $15 > \theta > 13^\circ$ . Data collection was done on an Enraf-Nonius CAD-4 diffractometer, using Mo  $K\alpha$  radiation and a graphite monochromator by  $\omega$ -2 $\theta$  scans designed for  $I \approx 50\sigma(I)$ , with a maximum scan time of 120 s. The scan rates varied  $0.39 - 4.0^\circ \text{ min}^{-1}$ . Reflections having  $2 < 2\theta < 53^\circ$  with  $0 \leq h \leq 4$ ,  $0 \leq k \leq 11$ ,  $-34 \leq l \leq 34$  were measured and corrected for background, Lorentz, and polarization effects; no absorption corrections were made. Redundant  $0kl$  and  $0k\bar{l}$  were averaged,  $R_{\text{int}} = 0.025$ . Standard reflections were 200, 020, 0,0,10, giving  $\pm 2.3\%$  maximum random variation. The structure was solved by direct methods using *MULTAN*<sup>78</sup> and refined by full-matrix least squares based on  $F$ , using 1179 data with  $I > \sigma(I)$  and weights  $w = \sigma^{-2}(F_o)$ , with the Enraf-Nonius *SDP* package<sup>258</sup>. Non-H atoms were refined anisotropically and the H-atoms were located by  $\Delta F$  and refined isotropically. The secondary extinction coefficient was  $9.6(10) \times 10^{-7}$ . Final  $R = 0.049$ ,  $R_w = 0.041$ ,  $S = 1.744$  for 169 variables. The maximum shift in the final cycle was  $0.09\sigma$  and the largest residual density was  $0.20 \text{ e Å}^{-3}$  and the minimum was  $-0.24 \text{ e Å}^{-3}$ . Atomic coordinates and equivalent isotropic thermal parameters can be found in reference

259b. Formula:  $2\text{C}_5\text{H}_6\text{N}^+\cdot\text{C}_2\text{H}_2\text{O}_4$ ,  $M_r = 428.4$ , monoclinic,  $P2_1/n$ ,  $a = 3.725(1)$ ,  $b = 8.908(2)$ ,  $c = 26.842(4)\text{\AA}$ ,  $\beta = 92.94(2)^\circ$ ,  $V = 889.5(6)\text{\AA}^3$ ,  $Z = 2$ ,  $D_x = 1.599\text{ gcm}^{-3}$ , Mo  $K_\alpha$ ,  $\lambda = 0.71073\text{\AA}$ ,  $\mu = 1.31\text{ cm}^{-1}$ ,  $F(000) = 444$ ,  $T = 296\text{ K}$ ,  $R = 0.049$  for 1179 observations (of 1838 unique data).

### Discussion

**Dipyridinium oxalate-oxalic acid.** Contrary to the  $\text{p}K_a$  based conclusions, *one oxalic acid donates two protons to pyridine bases rather than two oxalic acids giving up one proton each!* Figure 19 illustrates that the structure contains pyridinium ions, oxalate ions, and oxalic acid molecules. The oxalate and oxalic acid moieties are hydrogen bonded in a linear fashion with the pyridinium ions hydrogen bonded to the oxalate in a trans orientation. Thus, each oxygen of the oxalate moiety is hydrogen bonded to either an oxalic acid or a pyridinium ion. A structure containing both oxalic acid molecules and oxalate ions has been reported.<sup>260</sup> All of the heavy atoms of the pyridinium ion lie within  $0.001(2)\text{\AA}$  of a common plane, and the acidic proton bonded to it lies within  $0.01(2)\text{\AA}$  of that plane. This pyridinium cation donates a hydrogen bond to O(4) of the oxalate anion with an N-O distance of  $2.716(1)\text{\AA}$ . Theoretical calculations for the pyridine-HF dimer indicated that the favored geometry for the angle  $\angle\text{FHN}$  is  $180^\circ$ , i.e. a linear hydrogen bond.<sup>261</sup> However, in this case, the corresponding angle ( $\angle\text{OHN}$ ) is only  $152(2)^\circ$ . Of probable importance in causing this non-linearity is the somewhat longer contact between pyridinium N and O(3') of the same oxalate anion. Indeed, the contact between the pyridinium and oxalate ions may best be thought of as an asymmetrically bifurcated hydrogen bond.<sup>262</sup>

**Dipyridinium bis(hydrogen oxalate)-oxalic acid.** The structure contains hydrogen oxalate ions hydrogen bonded in chains along the  $b$  axis. These chains are linked by

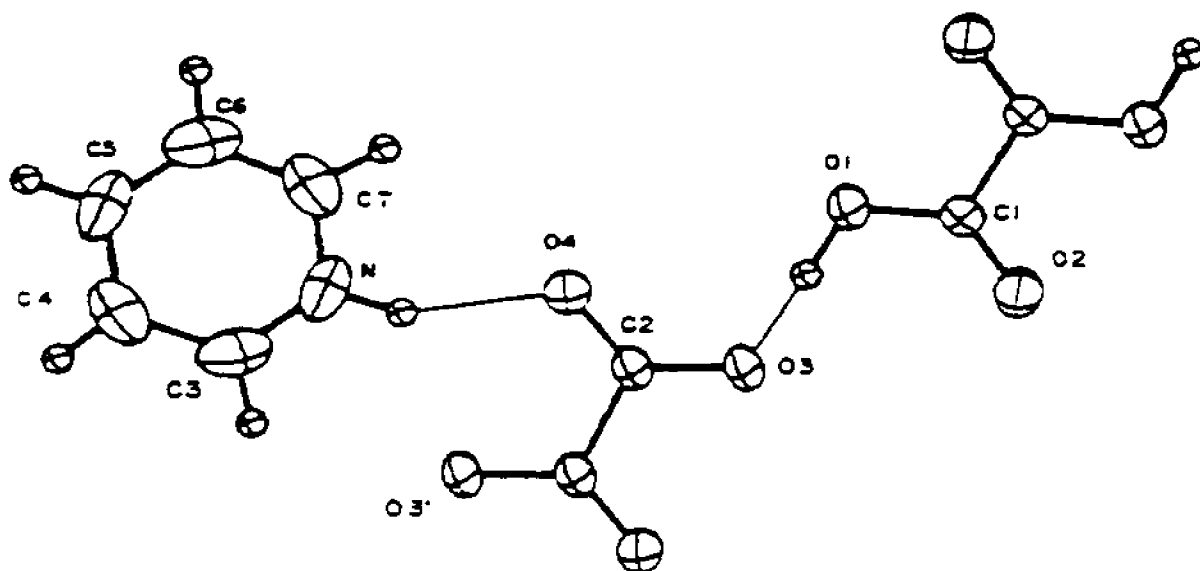


Figure 19. ORTEP Drawing of  $2\text{C}_5\text{H}_6\text{N}^+\cdot\text{C}_2\text{O}_4^{2-}\cdot\text{C}_2\text{H}_2\text{O}_4$ .

oxalic acid molecules donating hydrogen bonds to O(2) of hydrogen oxalate ions in neighboring parallel chains. The resulting non-planar, hydrogen-bonded sheets are stacked along the  $[10\bar{1}]$  direction. Pyridinium ions are hydrogen bonded to the carbonyl O-atom of each hydrogen oxalate in this array. Figure 20 portrays an ORTEP drawing of **187**. Although most hydrogen oxalates are nearly planar this one is *not*, with a relatively large O(3)-C(6)-C(7)-O(1) torsion angle of  $14.9(4)^\circ$ .<sup>263-265</sup>

The pyridinium moiety is planar [maximum deviation  $0.004(3)\text{\AA}$ ] and forms a hydrogen bond to the carbonyl of the hydrogen oxalate [N-O(3)  $2.792(2)\text{\AA}$ , N-H-O  $138(2)^\circ$ ]. The pyridinium ion also forms a longer interaction with O(1) of the next hydrogen oxalate ion along the *b*-axis chain. This interaction has N $\cdots$ O(1) distance  $3.098(2)\text{\AA}$ , H(1N) $\cdots$ O(1) distance  $2.38(3)\text{\AA}$ , and N-H $\cdots$ O angle  $129(2)^\circ$ . This interaction is similar to that found between the pyridinium and oxalate species in **186** and may best be thought of as an asymmetric bifurcated hydrogen bond.

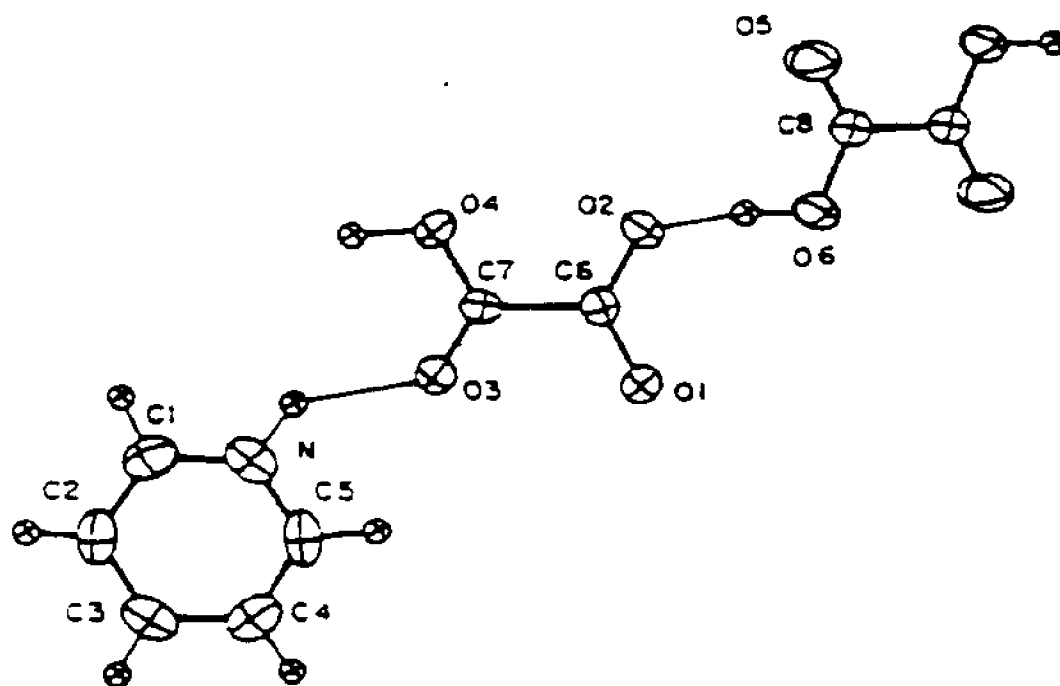


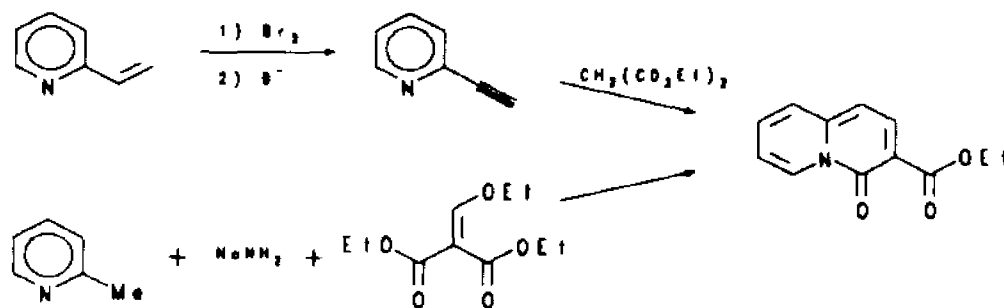
Figure 20. ORTEP Drawing of  $2\text{C}_5\text{H}_6\text{N}^+ \cdot 2\text{C}_2\text{HO}_4^- \cdot \text{C}_2\text{H}_2\text{O}_4$ .



## Chapter 6. An Improved Synthesis of 3-Methoxycarbonyl-4*H*-quinolizone via Palladium(II) Assistance.<sup>†</sup>

### Introduction

Since the parent and reduced quinolizine ring structures occur naturally both in the free state and as part of numerous alkaloids,<sup>266,267</sup> the herein facile synthesis of substituted 4*H*-quinolizones was pursued. Alkoxycarbonyl-4-quinolizones have generally been prepared by the condensation of the  $\alpha$ -anion of an activated picoline with ethoxymethylene derivatives of active methylene compounds.<sup>267b-d</sup> Thus, 1-methoxycarbonyl-3-ethoxycarbonyl-4-quinolizone was prepared from methyl 2-pyridylacetate and diethyl ethoxymethylidenemalonate in 73% yield.<sup>268</sup> Unfortunately attempted mono-dealkoxycarbonylation of 1,3-disubstituted 4-quinolizones gave exclusively the more stable 1-substituted product. Bohlmann reported the synthesis of 3-ethoxycarbonyl-4-quinolizone by reaction of the  $\alpha$ -anion of 2-picoline, generated in situ from 2-picoline with  $\text{NaNH}_2$ , with the above mentioned electrophile; the yield was unreported.<sup>269</sup> Another synthesis involved initial generation of 2-ethynylpyridine, prepared in two steps from 2-vinylpyridine, which was then condensed with diethyl malonate to give the desired quinolizone in a meager 8% overall yield from the

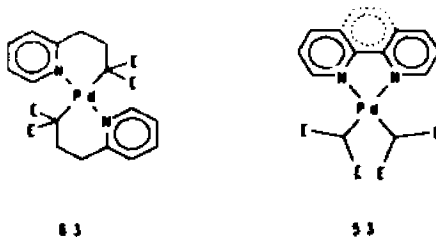


Scheme III. Previous Syntheses of 3-Carboalkoxy-4*H*-quinolizones.

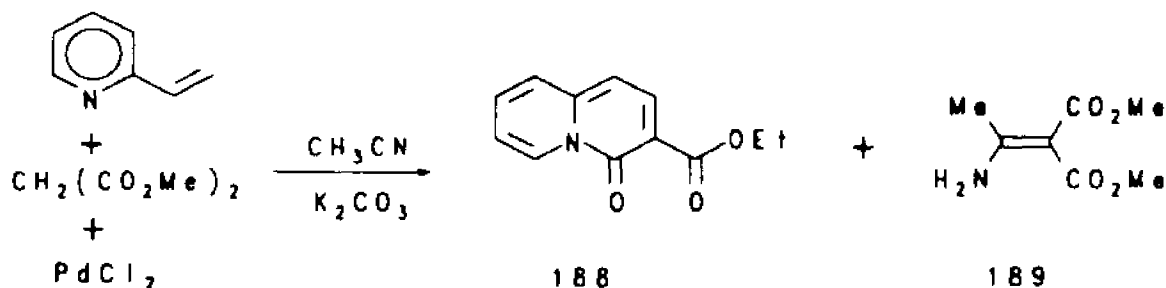
<sup>†</sup>Newkome, G. R.; Theriot, K. J.; Fronczek, F. R.; Casten, C. C. *Heterocycles*, 1988, 27, 385.

olefin<sup>270</sup>.

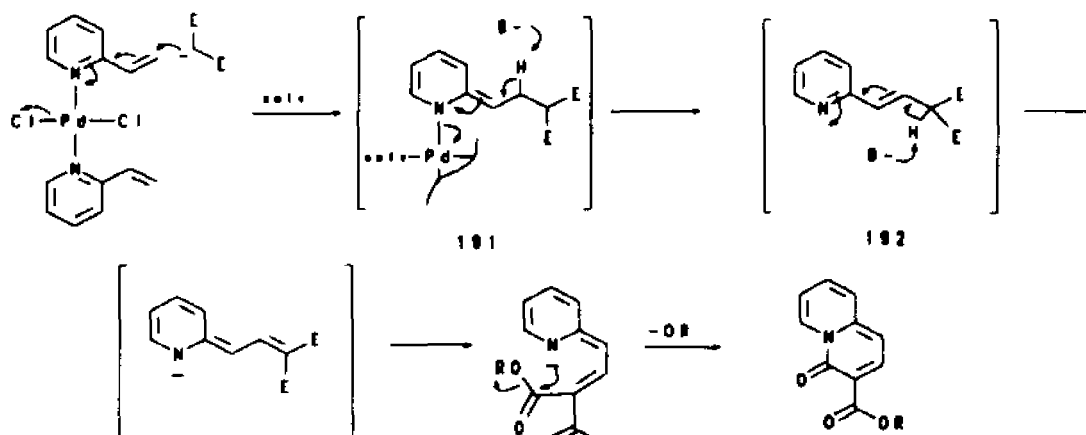
The original synthesis of **63b** ( $X = CH$ ) was accomplished by the Michael addition of 2-vinylpyridine with sodiummalonate, without transition metal catalysis, followed by Pd(II)-*N*-complexation and subsequent cyclometalation;<sup>271</sup> in addition, *C*-malonato Pd(II) complexes **53** were also prepared.<sup>272</sup> In an attempt to prepare **63b** from its



individual components (i.e. 2-vinylpyridine, dialkyl malonate and PdCl<sub>2</sub>) in a one-pot synthesis, the unanticipated **188** and **189** were isolated. Due to the very mild reaction conditions, it became apparent that Pd(II) was activating the vinyl group towards Michael addition. [In the absence of Pd(II), addition of malonate to 2-



vinylpyridine requires alkoxide, as base, in *refluxing* alcohol (ca. 80 °C).] To determine if the effect was an inductive one or if a Pd  $\pi$ -bond was present, bis(2-vinylpyridine)PdCl<sub>2</sub>, (**190**) was isolated by mixing 2-vinylpyridine and PdCl<sub>2</sub> in a 2:1 ratio (to avoid Cl-bridged dimer formation) in CH<sub>3</sub>CN; the desired complex **190** precipitated. An X-ray crystal structure determination of **190** clearly showed exclusive *N*-coordination and that *no Pd-vinyl interactions exist*. Thus the Pd(II) activation of



Scheme IV. Proposed Mechanism for the Formation of 3-Methoxycarbonyl-4H-quinolizone.

the olefin to nucleophilic addition must be an inductive electron withdrawing effect.

A mechanism which invokes palladium assistance for the formation of **188** is given in Scheme IV. In the reaction of **190** with methyl sodiomalonate, the electron withdrawing effect of Pd(II) on the pyridine ring caused an  $S_N2'$  reaction to proceed [rather than exclusive 1,2-addition as in the absence of Pd(II)] with sequential elimination of chloride ion from Pd(II) to give **191**. Abstraction of the acidic  $\beta$ -hydrogen of **191** afforded pyridine **192** with concomitant reduction of Pd(II) to Pd(0). Based on the fact that no Pd(0) was isolated from, or observed in, the reaction mixture, the Pd(0) may then have formed a  $\pi$ -complex with unreacted 2-vinylpyridine, which then decomposed on work-up. Subsequent loss of the labile allylic proton under the basic conditions and cyclization gave **188**. Although quinolizone **188** was obtained when other solvents were used (e.g. MeOH, EtOH, acetone, DMF, and Me<sub>2</sub>SO), DMF was the best solvent medium in that the highest yields (ca. 39%) were realized, although the reaction conditions were not optimized.

Although disorder in the crystal of **190** (Figure 21) prevented an accurate

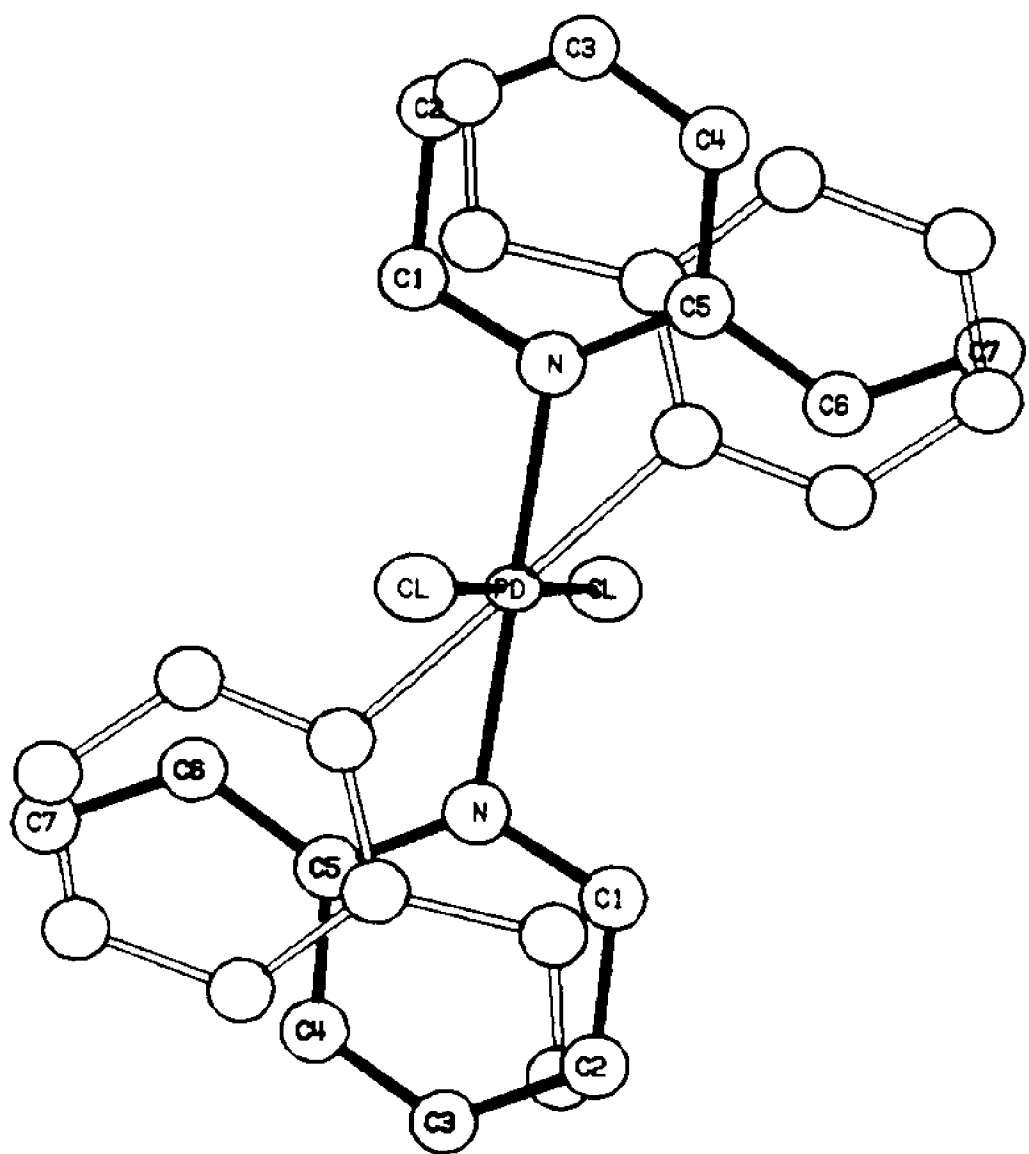


Figure 21. ORTEP Drawing of  $\text{PdCl}_2(\text{C}_7\text{H}_7\text{N})_2$ .

determination, several salient features were evident. There are no inter- or intramolecular Pd-vinyl interactions. The geometry around Pd is square planar with the two trans pyridine rings being nearly coplanar and both orthogonal to the line defined by Cl-Pd-Cl. The Pd-Cl bonds are 2.287(2) Å and Pd-N average 2.02(3) Å.

Because of the lack of precedence for the formation of **189** under such conditions, an X-ray crystal structure determination of **189** was undertaken to prove its solid state structure (Figure 22). It exists in the enamine form rather than the imine form as seen by the shortened C(2)-C(3) bond [1.394(2) Å]. The carboxylate trans to the amino group is not coplanar with the rest of the molecule and is oriented such that the torsion angle O(2)-C(4)-C(3)-C(2) is 135.6°; the rest of the molecule is essentially planar. The second *H*-atom on *N* could not be located although all other *H* positions are evident in difference maps. This *H*-atom is thought to be disordered in spite of the potential N-O(3) intramolecular contact of 2.613(2) Å. This structure determination supports the conformation predicted from vibrational spectroscopy.<sup>273</sup>

Quinolizone **188** is planar (Figure 23) and exists as the monohydrate with water forming a nearly symmetric bridge between O(1) and O(2). In the pyridine moiety, the C(1)-C(2) and C(3)-C(4) bonds are shortened [1.341(2) and 1.343(2) Å, respectively]. In the other ring the C(8)-C(9) distance is short [1.358(2) Å] and the C(9)-N bond long [1.468(2) Å]. The external angles about the ring carbonyl carbon {C(8)-C(9)-O(1) [129.18(14)°] and N-C(9)-O(1) [116.49(13)°]} indicate that the oxygen is tilted slightly toward the ring nitrogen perhaps because of *N*-electron delocalization into the ring and onto the oxygen although not directly between C(9)-N [1.468(2) Å].

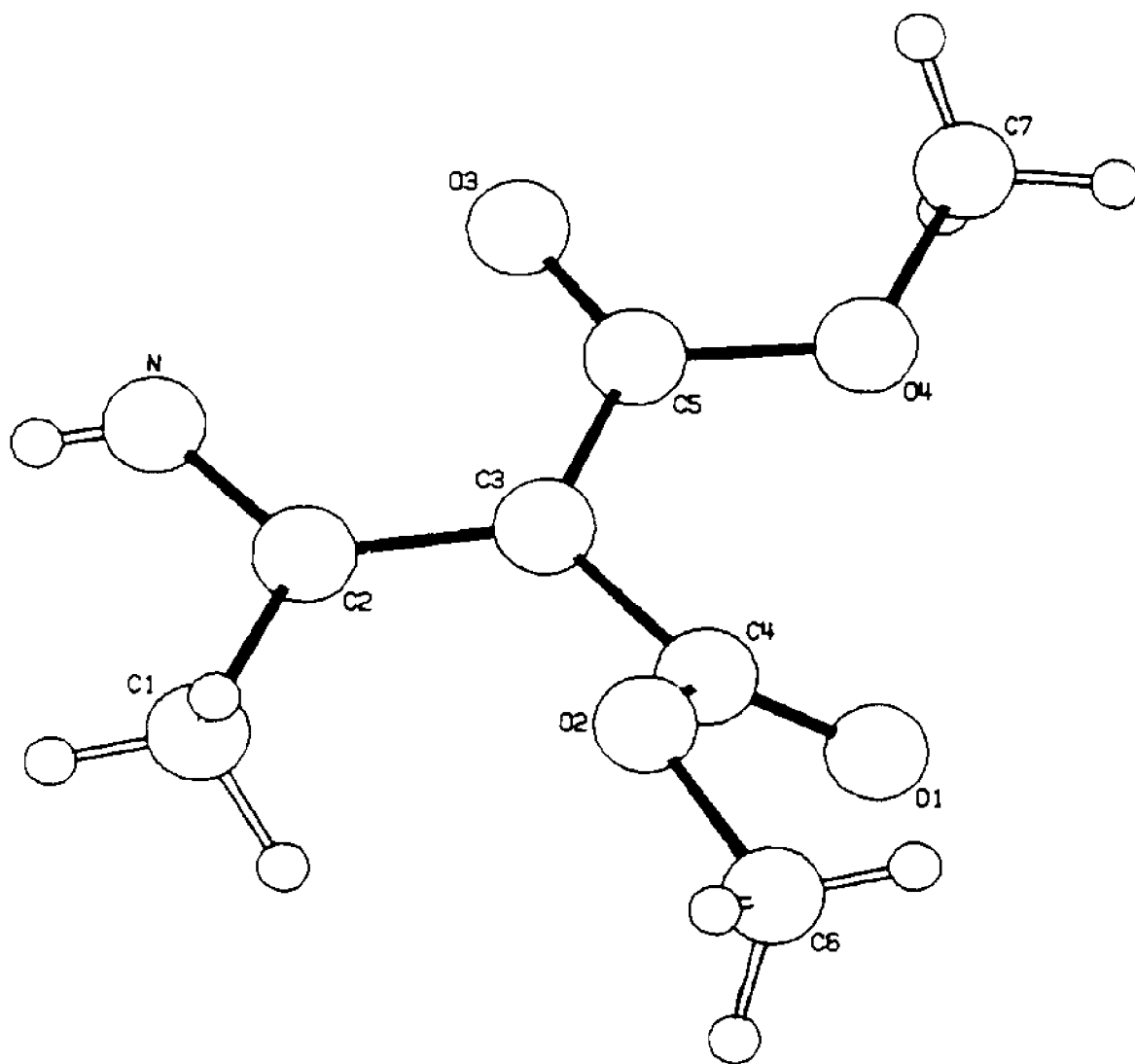


Figure 22. ORTEP Drawing of  $C_7H_{11}NO_4$ .

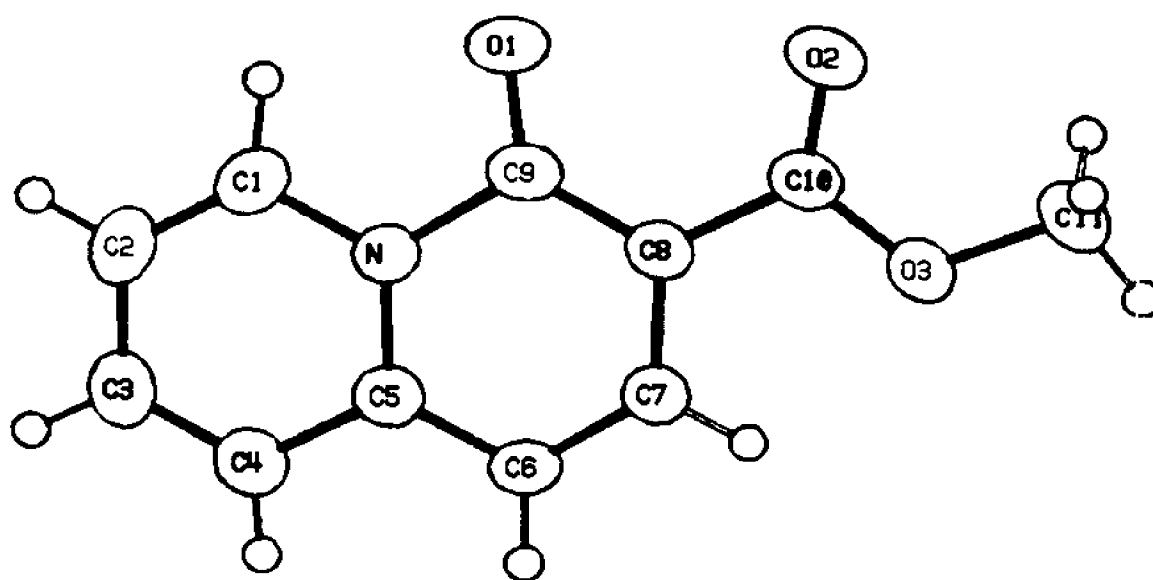


Figure 23. ORTEP Drawing of  $C_{11}H_9NO_3$ .

## Experimental

All melting points were taken in capillary tubes with a Thomas-Hoover Uni-melt apparatus and are uncorrected.  $^1\text{H}$  and  $^{13}\text{C}$  NMR were recorded on either an IBM NR/80 or IBM AF/100 spectrometer using  $\text{CDCl}_3$  as solvent (unless otherwise specified) with  $\text{Me}_4\text{Si}$  and  $\text{CDCl}_3$  as respective internal standards.  $^{13}\text{C}$  NMR data were assigned using selective  $^1\text{H}$  decoupled experiments. Mass spectral (MS) data (70 eV) were determined by Mr. D. A. Patterson on a Hewlett-Packard HP 5985 GC/mass spectrometer. Preparative thick-layer chromatography (ThLC) was performed on 20 x 40 cm glass plates coated with a 2-mm layer of Brinkman silica gel PF-254-366.

Intensity data for **188**, **189**, and **190** were collected on an Enraf-Nonius CAD4 diffractometer equipped with Mo  $\text{K}\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) and a graphite monochromator. The crystal of **189** was sealed in a capillary to prevent sublimation. Variable scan rates were employed in the  $\omega$ - $2\theta$  scans in order to achieve approximately equal relative precision for all observable data. One quadrant of data was collected for the monoclinic crystal, one hemisphere for the triclinic crystals.<sup>274</sup> Data reduction included corrections for background, Lorentz, and polarization effects. Absorption corrections for **190** were based on  $\psi$  scans of reflections near  $\chi = 90^\circ$ ; the minimum relative transmission coefficient was 61.24%. Equivalent data were averaged; data having  $I > 3\sigma(I)$  were used in the refinement for **189**, those having  $I > 0$  for **188** and **190**.

The structures of **188** and **189** were solved using MULTAN, that of **190** by heavy-atom methods. Refinements of **188** and **189** were full-matrix least squares based on  $F$  with weights  $w = \sigma^{-2}(F_o)$ , treating non-hydrogen atoms anisotropically, with H atoms located by  $\Delta F$  and refined isotropically. Disorder in **190** prevented routine refinement.



Only Pd and Cl atoms were treated anisotropically, while half-populated vinylpyridine ligand atoms were treated isotropically. Well resolved half-atoms in the disordered region were refined by full-matrix least squares, while positions of C2, C5, C7 and their equivalents in the alternate orientation were adjusted with the aid of difference maps. Ordered models in possible alternate space groups  $C2$  and  $C_c$  led to high correlations and did not lead to improved agreement with the data, and thus were abandoned. Final  $R$  factors for **188**, **189**, and **190** were 0.036, 0.049, and 0.076, respectively.

**Dichlorobis(2-vinylpyridine)palladium(II) (190).** Freshly distilled 2-vinylpyridine (181 mg, 1.72 mmol) was added to  $\text{PdCl}_2$  (132 mg, 740  $\mu\text{mol}$ ) in dry  $\text{CH}_3\text{CN}$  (30 mL) and stirred for 12 h at 25 °C. The precipitated complex was filtered and washed with a small amount of  $\text{CH}_3\text{CN}$  to give (74%) **190**, as a bright yellow solid: 214 mg; mp 178-180 °C (dec);  $^1\text{H}$  NMR  $\delta$  5.94 (d,  $\beta\text{-CH}_{\text{trans}}$ ,  $J_{\alpha,\beta\text{trans}} = 11.2$  Hz, 1H), 6.10 (d,  $\beta\text{-CH}_{\text{cis}}$ ,  $J_{\alpha,\beta\text{cis}} = 17.5$  Hz, 1H), 7.16-7.35 (m, 5-pyH, 1H), 7.56-7.64 (m, 3-pyH, 1H), 7.66-7.87 (m, 4-pyH, 1H), 8.59 (dd,  $\alpha\text{-CH}$ ,  $J_{\alpha,\beta\text{cis}} = 17.5$ ,  $J_{\alpha,\beta\text{trans}} = 11.2$  Hz, 1H), 8.98 (ddd, 6-pyH,  $J_{5,6} = 5.6$ ,  $J_{4,6} = 1.7$ ,  $J_{3,6} = 0.8$  Hz, 1H).

**3-Methoxycarbonyl-4H-quinolizone (1).** Method A - Reaction in DMF. Dimethyl malonate (823 mg, 6.24 mmol) and anhydrous  $\text{K}_2\text{CO}_3$  (1.62 g, 11.7 mmol) were added to dichlorobis(2-vinylpyridine)palladium(II) (302 mg, 6.24 mmol) in reagent grade DMF (50 mL). After stirring at 50 °C for 12 h, the solvent was removed in vacuo, the residue dissolved in  $\text{CHCl}_3$  and filtered. The  $\text{CHCl}_3$  soluble material was purified by ThLC eluting with 5% MeOH/ $\text{CHCl}_3$  to give (39%) **188**, as yellow microcrystals: 61 mg; mp 116.5-117.3 °C (pet. ether);  $^1\text{H}$  NMR  $\delta$  3.95 (s,  $\text{CH}_3$ , 3H), 6.66 (dd, 1-quinH,  $J_{1,2} = 8.5$ ,  $J_{1,8} = 0.6$  Hz, 1H), 7.20 (ddd, 6-quinH,  $J_{5,6} = 7.3$ ,  $J_{6,7}$

= 4.8,  $J_{6,8}$  = 3.4 Hz, 1H), 7.57-7.65 (m, 7,8-quinH, 2H), 8.41 (d, 2-quinH,  $J_{1,2}$  = 8.5 Hz, 1H), 9.40 (dd, 5-quinH,  $J_{5,6}$  = 7.3,  $J_{5,7}$  = 0.9 Hz, 1H);  $^{13}\text{C}$  NMR  $\delta$  52.0 ( $\text{CH}_3$ ), 101.6 (C1), 115.9, 124.7 (C7 & C8), 133.0 (C5), 140.4 (C2), 166.1 (3-CO), 167.1 (C4); MS  $m/z$  203 (10), 188 (8), 172 (11), 160 (21), 132 (37), 106 (39), 78 (100).

**Method B - Reaction in  $\text{CH}_3\text{CN}$ .** Using the same procedure as with DMF, gave (20%) **188** and methyl 3-amino-2-methoxycarbonyl-2-butanoate (**189**) as colorless microcrystals: mp 83.5-84.5 °C (lit.<sup>273</sup> mp 83-84 °C); Subl. 50°C (2 mm);  $^1\text{H}$  NMR  $\delta$  2.15 (s,  $\text{CCH}_3$ , 1H), 3.71 (s,  $\text{OCH}_3$ , 1H), 3.74 (s,  $\text{OCH}_3$ , 1H);  $^{13}\text{C}$  NMR  $\delta$  22.2 ( $\text{CCH}_3$ ), 51.1 ( $\text{OCH}_3$ ), 51.7 ( $\text{OCH}_3$ ), 164.1 (CO), 169.0 (CO); MS  $m/z$  173 (48), 142 (100), 141 (88), 110 (26), 83 (22).

## Summary and Conclusions

**Organoplatinum Complexes.** Several new organoplatinum(II) C-malonato complexes of two types have been synthesized and fully characterized by  $^1\text{H}$  and  $^{13}\text{C}$  NMR and IR. The first type is a cyclometalated complex of pyridinyl ligands possessing pendants at the 2-position with terminal malonate groups capable of forming either a five- or six-membered C,N-chelate. These complexes have trans carbon-metal bonds and have also been characterized by X-ray crystal structure determinations.

The second type of complex is an *N,N'*-chelate of dipyridine or phenanthroline in which platinum is bonded to the central carbons of two different dimethyl malonate ligands. The reactivity of these cis complexes was investigated and they were found to be rather inert toward reagents known to react with organoplatinum complexes such as acyl halides and vinyl ketones; methyl iodide did react with them but a complex mixture was obtained. These *N,N'*-chelates were easily oxidized by either  $\text{Br}_2$  or  $\text{Cl}_2$  to give the corresponding Pt(IV) complexes which, although possessing cis alkyl groups, were stable and only underwent reductive elimination under basic conditions; interestingly, this oxidation could also be accomplished by Cu(II) halides. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of the Pt(IV) complexes were used to establish the fact that oxidation had occurred via the  $^1J_{\text{PtC}}$  and  $^1J_{\text{PtH}}$  coupling constants which were 30% less than the corresponding Pt(II) coupling constants as expected.

An interesting feature of the  $^{13}\text{C}$  NMR spectra was that where two different pathways were possible for Pt-C coupling to a particular carbon, the observed coupling constant was the sum of the two constants.

Future endeavors should focus on the potential anti-tumor activity of the cis

complexes which possess the "cis diammine" structure important in complexes that are active against tumors. Other possibilities include catalysis in hydrogenation or carbonylation reactions and, for the cis complexes, modifications utilizing the remaining acidic hydrogen on malonate.

**Cyclometalated Palladium Complexes.** Very few examples of cyclometalated 2-vinylpyridines have been reported, but, by the utilization of  $\alpha$ -substituted 2-vinylpyridine derivatives, novel cyclometalated Pd(II) dimers were readily synthesized. The  $\alpha$ -substituent on the ligand facilitates cyclometalation by stabilizing the intermediate carbocation which is formed by electrophilic attack of the metal on the alkenyl moiety. These dimers were readily cleaved by pyridine or triphenylphosphine and the structure of one of these monomers was proven by an X-ray crystal structure determination which showed the existence of the metal-alkenyl bond.

Future work should include the use of other metals for cyclometalation and synthetic transformation of both the alkenyl moiety and the  $\alpha$ -substituent.

**Functionalization of Methyl Naphthyridines.** The methyl group(s) of 2-methyl- and 2,7-dimethyl-1,8-naphthyridine were oxidized to hydroxymethyl moieties by a three-step synthesis. The methyl group was oxidized with NCS to a trichloromethyl group followed by  $\text{H}_3\text{PO}_4/\text{MeOH}$  hydrolysis to give the methyl ester which was then reduced to the hydroxymethyl functionality by  $\text{NaBH}(\text{OMe})_3$ , which does not readily reduce less reactive esters. Because of the enhanced reactivity of the naphthyridine system, reagents that were used on other heterocycles [e.g.  $\text{H}_2\text{SO}_4$ , and  $\text{NaBH}_4$ , (and NCS/ $\text{CCl}_4$  for 2-methyl-1,8-naphthyridine)] could not be used on naphthyridine.

Possible extensions of this work include investigating the complexation properties of the functionalized naphthyridines and incorporation of the di-functionalized derivative into macrocyclic ligand systems.

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## VITA

Kevin J. Theriot was born in Houma, Louisiana on June 16, 1958. He completed secondary education at H. L. Bourgeois High School in Gray, Louisiana where he graduated in May, 1976. The author received a B.S. in chemistry from Northeast Louisiana University in Monroe, Louisiana in May, 1980. From there he moved to Louisiana State University where he worked as a graduate student while completing requirements for the doctoral degree. He has accepted a position as research chemist at Ethyl Corporation (Technical Center) in Baton Rouge, Louisiana.

## List of Publications

1. "[2,2-Di(2-pyridyl)-1,3-dioxolane-N,N']dichloropalladium(II), [PdCl<sub>2</sub>(C<sub>13</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub>)]" Newkome, G. R.; Gupta, V. K.; Theriot, K. J.; Ewing, J. C.; Wicelinski, S. P.; Huie, W. R.; Fronczek, F. R.; Watkins, S. F. *Acta Cryst.* **1984**, *C40*, 1352.
2. "Dipyridinium oxalate-oxalic acid" Newkome, G. R.; Theriot, K. J.; Fronczek, F. R. *Acta Cryst.* **1985**, *C41*, 1642.
3. "Synthesis of Metal Paddlanes: X-ray Structure Determination of bis(Methyl nicotinate)copper(II) acetate Dimer" Newkome, G. R.; Theriot, K. J.; Gupta, V. K.; Balz, R. N.; Fronczek, F. R. *Inorg. Chim. Acta* **1986**, *114*, 21.
4. "Dipyridinium bis(hydrogen oxalate)-oxalic acid" Newkome, G. R.; Theriot, K. J.; Fronczek, F. R. *Acta Cryst.* **1986**, *C42*, 1539
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8. "Chemistry of Heterocyclic Compounds. Part 132. Metallocyclic Complexes of Palladium(II) and Platinum(II) Containing Six- and Seven-membered Chelate

- Rings" Newkome, G. R.; Evans, D. W.; Kiefer, G. E.; Theriot, K. J. *Organometallics* **1988**, *7*, 2537.
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  10. "Synthesis and Characterization of Metalated and Cyclometalated Pt(II) and Pt(IV) Complexes of  $\beta$ -Diesters" Newkome, G. R.; Theriot, K. J.; Fronczek, F. R.; Villar B. In press, *Organometallics* **1989**.
  11. "Synthesis and Characterization of Novel Pd(II) Cyclometalated Complexes of 2-Vinylpyridine Derivatives" Newkome, G. R.; Theriot, K. J.; Cheskin B. K.; Evans, D. W. Submitted to *Organometallics*, **1989**.
  12. "Methyl Functionalization of 2-Methyl- and 2,7-Dimethyl-1,8-Naphthyridine" Newkome, G. R.; Theriot, K. J.; Spruell, P. A. In preparation for submission to *J. Org. Chem.*, **1989**.
  13. "Palladium(II) Assisted Synthesis of 3-Substituted-4-quinolizones" Newkome, G. R.; Theriot, K. J.; Fronczek, F. R.; presented at the Tenth International Congress of Heterocyclic Chemistry, University of Waterloo, Ontario, Canada, Aug. 11-16, 1985.
  14. "Synthesis and Structural Analysis of Organoplatinum(II) Complexes Possessing  $sp^3$ -Carbon-Metal Bonds" Newkome, G. R.; Theriot, K. J.; Fronczek, F. R.; Kiefer, G. E.; Evans, D. W.; presented at the 190<sup>th</sup> American Chemical Society National Meeting, Chicago, IL, Sept. 8-13, 1985.

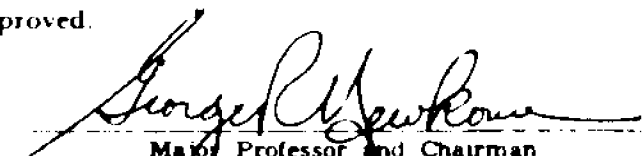
# DOCTORAL EXAMINATION AND DISSERTATION REPORT

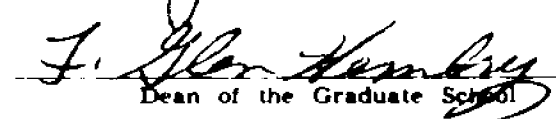
**Candidate:** Kevin J. Theriot

**Major Field:** Chemistry

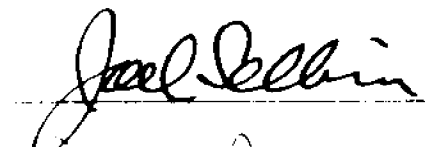
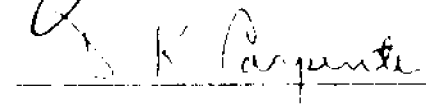
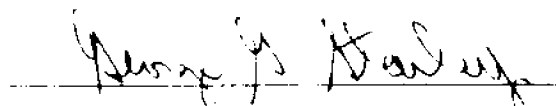
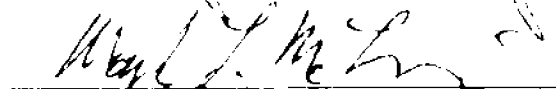
**Title of Dissertation** Syntheses of Organometallic Platinum(II), Platinum(IV),  
and Palladium(II) Complexes and Methyl Functionalization  
of 2-Methyl- and 2,7-Dimethyl-1,8-Naphthyridine

Approved.

  
Major Professor and Chairman

  
Dean of the Graduate School

## EXAMINING COMMITTEE:

**Date of Examination:**

July 24, 1989